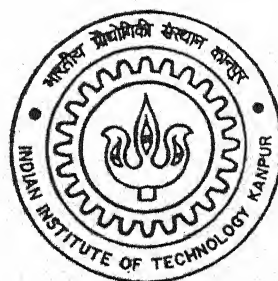# PREPARATION OF NANOSIZED ZIRCONIA POWDERS AND THEIR CHARACTERIZATION A DYNAMIC LIGHT SCATTERING INSTRUME

By

ARINDAM PAUL

MATERIALS SCIENCE PROGRAMME

Indian Institute of Technology Kanpu

JULY, 2003

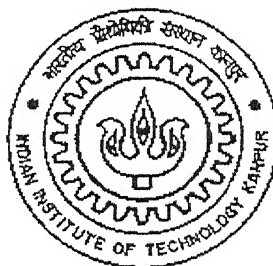# PREPARATION OF NANOSIZED ZIRCONIA POWDERS AND THEIR CHARACTERIZATION BY A DYNAMIC LIGHT SCATTERING INSTRUMENT

A Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of

MASTER OF TECHNOLOGY

In

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By

ARINDAM PAUL

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INDIAN INSTITUTE OF TECHNOLOGY KANPUR
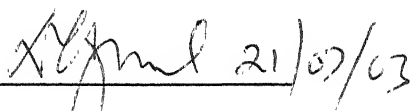
JULY, 2003

CERTIFICATE

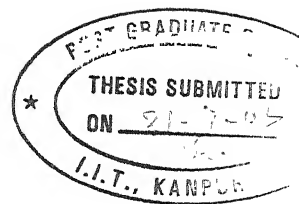It is certified that the work contained in the thesis entitled *"Preparation of Nanosized Zirconia Powders and Their Characterization by a Dynamic Light Scattering Instrument"*, by *Arindam Paul,* has been carried out under my supervision and that this work has not been submitted elsewhere for any degree.

July 2003

Dr. D. C. Agrawal

Professor

Materials Science Programme

Indian Institute of Technology Kanpur

India

DEDICATED

TO

MY   PARENTS

ACKNOWLEDGEMENT

and Sudip. They have tried to make me learn how to tackle a vulnerable period in life and also inculcate within me a real sense of pragmatism. I am really fortunate to get them as my *friend* in my llife. I would also like to thank my schoolmate Ranajit for continuously encouraging me in my studies.

I wish to give a heartful thanks to my kakima (Debju's mother) for her delicious Bengali dishes. It always made mc feel at home here.

I am highly indebted to Swaraj who helped me tremendously during my last stage of thesis preparation. It wouldn't be possible for me to complete my thesis within the stipulated time without him. No word is enough to express my gratefulness to him.

The unbreakable patience and silent support of my parents and also continuous encouragement from Guha family was always a constant source of inspiration.

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Arindam Paul

July 2003

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ABSTRACT

Use of nanopowders as precursors for ceramics such as zirconia can lead to significant improvement in properties. Although several methods have been reported in the literature for preparation of monodispersed, nanosized zirconia powders, but wet chemical routes via hydrolysis of aqueous solution of the metal salt have been found to be the simplest.

In the present study, spherical, nanoparticles of hydrous zirconia with a narrow size distribution have been prepared by microwave heating of zirconyl chloride solution-isopropanol mixture using hydroxypropyl cellulose (HPC) as a surfactant. As the temperature of the starting solution increases, precipitation occurs because of the decrease of solubility of the salt due to decrease in the dielectric constant of the medium. Effect of various factors like concentration of $ZrOCl_2,8H_2O$ and concentration of HPC on size and morphology of the particles has been extensively studied. It has been possible to systematically vary the average particle size of the prepared powders between 40 nm and 280 nm by control of these parameters. TEM results reveals that particle size of hydrous zirconia can be decreased by lowering the salt concentration and increasing the HPC concentration (upto a certain value) and particles of sizes as small as 40 nm can be produced at salt and HPC concentration of 0.005M and 21.25 micromolar (1.71×10^{-3} gm/cc) respectively.

In the present study, in addition to TEM, dynamic light scattering (DLS) technique has also been used for the characterization of ZrO_2 particles. For DLS technique a newly procured instrument called as High Performance Particle Sizer (HPPS) has been employed. For standardizing and proper calibration of this instrument, three sets

of sample eg. standard latex sphere, sumitomo alumina and TOSOH-ZrO_2 powders are used. It has been found that running of HPPS in the normal mode of measurement, accurate measurement of the viscosity of the suspending liquid, use of filtered suspension medium and use of well-dispersed suspensions are necessary to obtain correct result by HPPS.

The as prepared hydrous zirconia particles are found to have larger size when measured by HPPS as compared to TEM. This is attributed to presence of a surfactant/water layer at the surface of the particles.

The crystallization of the as-prepared amorphous hydrous zirconia particles is studied by calcination at 200^0, 400^0 and 600^0C respectively. The crystallized phase is found to be is monoclinic. The particle size does not change much upon cacination as observed by TEM result. The surface area of the particles decreases with increase in calcination temperature indicating that only the surface porosity sealed off.

CHAPTER 1

INTRODUCTION

1.1 ADVANCED CERAMICS

1.1.1 Zirconia: General

Advanced ceramic materials are in high demand for use in structural and functional applications. Monodispersed, ultrafine (i.e. submicron to nanosize) ceramic particles are important building blocks that are used in the fabrication of advanced ceramic materials having improved properties (mechanical, electrical, optical, magnetic, thermal, ionic conducting, and catalytic). Synthesis of high quality ultrafine powders with required characteristics in terms of their size, morphology, microstructure, composition purity, crystallinity etc. are of great interest for practical applications. These characteristics of precursor powders significantly affect the later stage processing and sintering properties and eventually determine the microstructure and performance of the final ceramic materials.

Zirconia ceramics are of great technological interest due to their unique properties. These are good mechanical strength, high fracture toughness and hardness, high refractoriness and corrosion resistance, high melting point, high thermal conductivity at higher temperature, ionic conduction and thermal stability and resistance to thermal shock[1]. Zirconia is an important component in diverse applications such as structural, ceramic engine parts, cutting and abrasive tools, sensors/probes (oxygen sensors), solid oxide fuel cell[2] and thermal barrier coatings, ceramic colors, piezoelectrics etc.

ZrO$_2$ is normally found in the naturally occurring mineral, baddeleyite which contains about 80% ZrO$_2$. The major impurities in this mineral are usually TiO$_2$, SiO$_2$, Fe$_2$O$_3$ etc. The other main source of ZrO$_2$ is zircon (ZrSiO$_4$) that occurs as secondary deposits in India, Australia and U.S [3]. ZrO$_2$ has three allotropes: monoclinic, tetragonal and cubic. At room temperature zirconia has a monoclinic baddeleyite structure, which is stable below 1170^{0}C. During cooling, the tetragonal phase (t) transforms diffusionlessly to a metastable monoclinic phase (m) at the martensitic temperature (T_0^{t-m}), which is accompanied with a considerable volume expansion (3-5%) and a shear strain (1-7%)[4]. Similarly on heating the m form changes to t phase at the austenite temperature above (T_0^{t-m}), without any compositional changes. At temperature of approximately 2370^{0}C, the tetragonal phase transforms into cubic fluorite structure that is stable up to the melting point (2680 $\pm$ 15 ^{0}C) [5]. In other words

$$\text{Baddeleyite (m-ZrO}_2\text{)} \underset{950^0C}{\overset{1150^0C}{\rightleftarrows}} \text{Tetragonal (t-ZrO}_2\text{)}$$

$$\xrightarrow{2370^0C} \text{Cubic (c- ZrO}_2\text{)} \xleftrightarrow{2680^0C} \text{Liquid (}l\text{)}$$
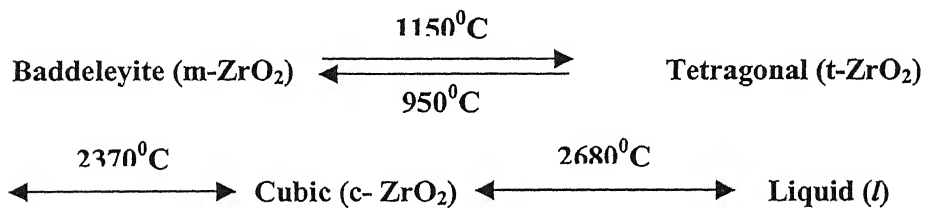
Due to large volumetric and shear strain during martensitic transformation between t $\longrightarrow$ m phases, pure (i.e. undoped) zirconia ceramic undergoes catastrophic failure. Due to this spontaneous failure on cooling, fabrication of large, pure zirconia ceramics becomes impossible. To overcome this difficulty, different amount of structure-stabilizing oxides (dopants) e.g. CaO, MgO, Y$_2$O$_3$, Gd$_2$O$_3$ etc. are added to ZrO$_2$ in such a fashion so that stabilizing ions are homogeneously distributed in the crystal structure of zirconia. Generally addition of 16 mol% CaO, 16 mol% MgO, 8 mol% Y$_2$O$_3$ or 10 mol% Gd$_2$O$_3$ is needed to form

transformation from room temperature up to 2500^0C. Also cubic phase has highest conductivity followed by tetragonal phase. Lower amount of additive oxides result in partially stabilized zirconia (PSZ) in which three phases may coexist in different amounts.

1.1.2 Importance and applications of nanocrystalline zirconia

Because of the very fine grain sizes, nanocrystalline zirconia exhibit a variety of properties that are different and considerably improved in comparison with those of conventional coarse grained zirconia. Some of the advantages are given below:

i) Diffusivity and sinterability are expected to be enhanced in comparison with coarse grained crystalline zirconia.

ii) The electrical, optical and chemical properties are superior than in the conventional coarse grained structure.

iii) Due to its fine grain size it has an improved forming characteristic that is an advantage over coarse grained structure.

iv) Improved mechanical properties and increased wear resistance.

v) Better physical-optical properties due to enhanced control over fine particles.

1.2 PREPARATION OF ZIRCONIA POWDERS BY VARIOUS CHEMICAL ROUTES

Ceramic powders should have the following physical and chemical characteristics: i) smaller particle size (micron to nano range) and narrow particle size distribution, ii) minimum degree of agglomeration (nearly monodispersed), iii) high

chemical purity, iv) maximum bulk particle density, v) controlled surface chemistry etc. Conventional ceramic powders processing routes (grinding, ball milling etc.) have been associated with many disadvantages like contamination, phase inhomogeneity, composition fluctuation etc. Therefore, in order to get rid of these problems, various chemical routes like sol-gel, sonochemistry, precipitation techniques etc. are of great interest.

1.2.1 Powder Preparation by sol-gel method

The sol-gel method using alkoxides as precursor materials is a very popular approach for preparation of monodispersed ceramic powder. Wang et al.[6] have studied the sol-gel method by dissolving zirconium n-butoxide in absolute ethanol under continuous stirring and then adding hydrolysis agent (NH$_4$OH) till pH became ~10. After that a small amount of water was added and the solution was stirred continuously until gelling. The gel was subsequently dried at room temperature in a vacuum for 24 hours. Then these gel powders were subjected to annealing at 400^0, 600^0 and 800^0C for 4 hours in air. Nanocrystalline zirconia with coexisting monoclinic and tetragonal phases with an average crystallite size ranging from 6 to 36nm was obtained. They have also found that the fractions of the phases change with annealing temperature. At 400^0C the main phase was tetragonal. But when temperature was increased from 400^0 to 800^0C, the tetragonal fraction decreased (from 84 to 11.9 wt%) while the monoclinic phase concentration increased (more than 80 wt% at 800^0C). This synthesis method leads to formation of t and m phase without cubic phase and irreversible phase transformation from t $\longrightarrow$ m occurs during calcination. This is in contrast with the result obtained by Yoshimura. M[7] where

transformation of low-temperature m phase to the t phase and then into cubic phase at higher temperature was reported.

C.L. Rebert et al [8] studied a colloid-emulsion route in order to prepare yttria stabilized zirconia (YSZ) powder by using commonly available inorganic salt such as zirconium chloride and yttrium nitrate as starting materials. The aqueous solution of these cationic salt, citric acid and ethylene glycol were mixed, subjected to heat treatment at 80^0C while stirring. A viscous polymeric product resulted due to complexation and esterification reactions, which was heat-treated at 100^0C overnight followed by calcination at 400^0C. Nanocrystalline, single phase YSZ powders with spherical morphology and about 1 μm aggregates size were formed by calcination of emulsion-derived precursor powder at 1000^0C for 2 hours. The authors have reported that the viscosity of the sol and concentration of metal salt didn't significantly influence the morphology of the particles. Effect of addition of different non-ionic (polyoxyethylenated alkytphenols family) surfactants and their concentration on aggregate size and morphology was extensively investigated. The authors found that an optimum concentration (8 vol%) of surfactant Igepal CA 630 was able to produce well-dispersed, spherical particles of 1 μm size.

.

1.2.2 Preparation by sonochemical approach

Sonochemistry is a very useful method in the preparation of nanoparticles. The mechanism of formation of particles through this route is discussed below:

In a liquid, acoustic cavitation due to chemical effects of ultrasound causes formation, growth and implosive collapse of bubbles. The implosive collapse of bubble generates localized hot spots through adiabatic compression or shock wave

formation within the gas phase of the collapsing bubble. During bubble collapse the extreme conditions are attained which are used for preparation of nanoparticles. The sonochemical reactivity consists of two distinct regions, i.e. the inside of the collapsing bubble and the interface between the bubble and the liquid.

Pang et al [9] investigated sonochemical method in preparing stable colloidal hydrous YSZ without the presence of a surfactant. Initially 0.08 mole of Y_2O_3 and 0.92 mole of $ZrO(NO_3)_2.xH_2O$ were dissolved in nitric acid and deonized water under heating and stirring, respectively. The solutions were mixed together and then NH_4OH was added dropwise into the solution under sonication that resulted in formation of as-prepared colloidal hydrous YSZ nanoparticles. This as-prepared YSZ aqueous suspension was not stable and coagulated after short time (due to condensation of surface hydroxyl groups) and yielded particle size of ~27 nm (measured by analytical ultracentrifugation, AUC) with distribution of 26%. So in order to stabilize it, water and ethanol washed product (as prepared hydrous YSZ) was again dissolved in absolute ethanol and sonicated for 30 minutes. This stable (with no detectable changes after 6 months) hydrous YSZ has particle size of ~2.8 nm (AUC result) with a size distribution of 13%. TEM micrographs (Fig 1.2.1a) also revealed monodispersed particles with sizes ~2.0 nm for ethanol treated sample.

The authors have proposed two roles of sonication in stabilizing the colloidal YSZ. First, the coagulated hydrous YSZ particles are broken into single particles by the shock wave formed under the sonication conditions. Secondly, partial dehydration of the as-prepared hydrous YSZ particles occurred at the interfacial regions around the cavitation bubbles during sonication in ethanol. The as-prepared amorphous powders were crystallized by solvothermal method (by using Parr Bomb at 250^0C, 48 hours) and calcination. Fig 1.2.1b shows TEM micrograph of
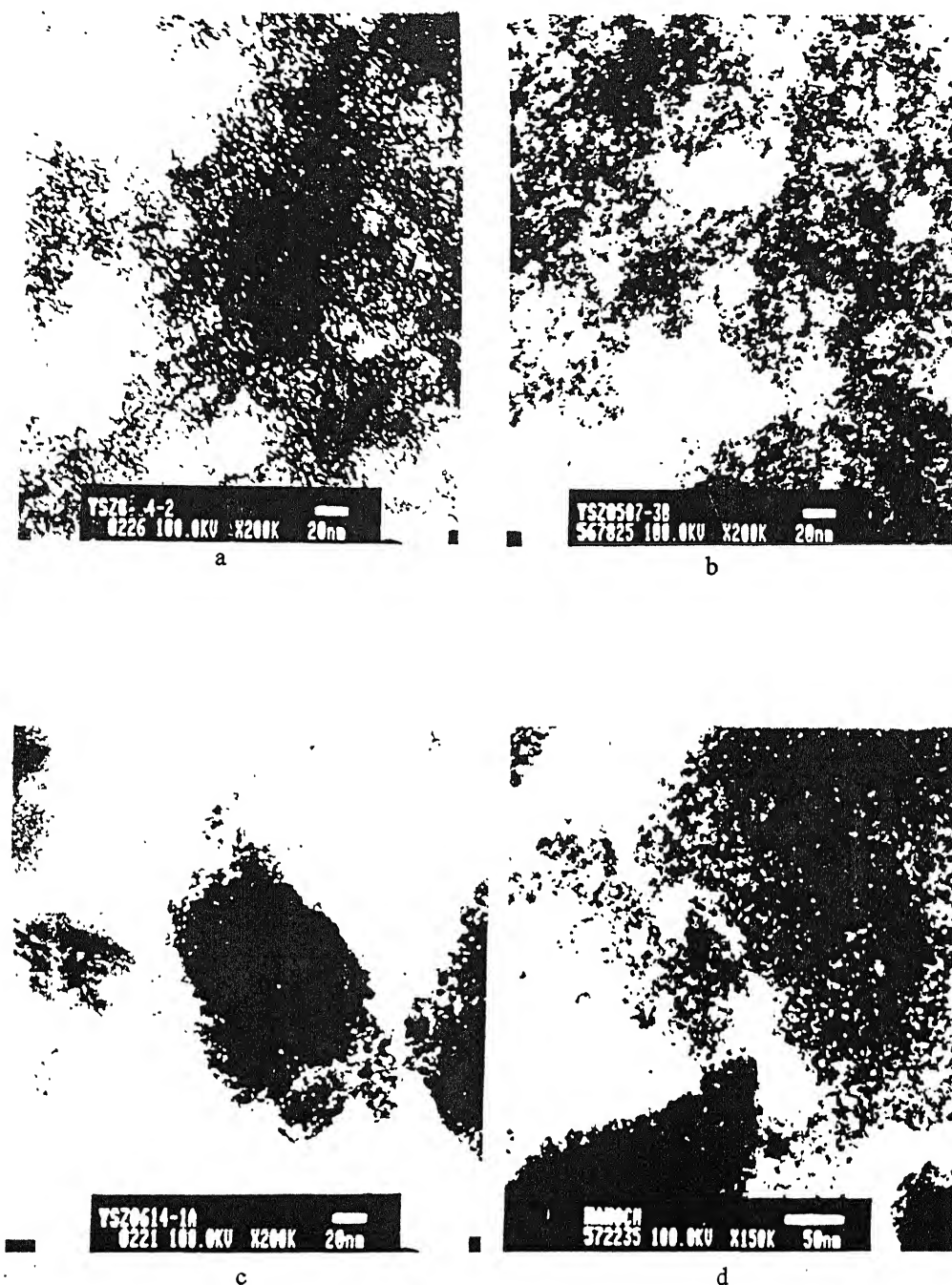
Fig 1.2.1 TEM micrographs of (a) the ethanol-treated hydrous YSZ sample, (b) the sample solvothermally treated in ethanol at 250^{0}C for 48 h, (c) the as-prepared sample calcined at 600^{0}C for 2 h, and (d) the ethanol-treated sample calcined at 600^{0}C for 2 h. [ref 9]

monodispersed particles (sizes ~5 nm) obtained by solvothermal method. Fig 1.2.1c

and d show calcined particles of the as-prepared (aggregate particles with sizes ~10

nm) and ethanol-sonicated product (narrower size distribution with average particle

size of ~6 nm) respectively.

1.2.3 Powder Preparation by Precipitation

Among the various chemical routes, precipitation of hydrous

zirconia from an aqueous solution containing zirconium salt is widely studied. The

hydrous zirconia can be precipitated in different ways, such as simply aging the

aqueous solution of zirconium salt at lower temperature for several days, adding of a

base i.e. either ammonium hydroxide or urea, uniform heating of an alcohol-water

solution containing salt of zirconium etc.

1.2.3.1 Precipitation by forced hydrolysis

Hu. et.al[1]. have studied forced hydrolysis method by preparing

aqueous solution of zirconyl chloride and incubating it at 100^0C for 3 days. The

authors obtained nearly cube-shaped, nano sized particles with narrow size

distribution (~50 nm average size) by using this technique. Fig 1.2.2 shows TEM

micrograph of hydrous zirconia particles produced from 0.075M $ZrOCl_2$ aqueous

solutions. Each of these particles was basically aggregate of small needle shaped

primary particles. They have also studied the effect of $ZrOCl_2$ concentration on the

secondary particle size and found that initially the particle size increased with $ZrOCl_2$

concentration (M) due to enhancement of hydrolysis kinetics reaction, but after a

critical concentration of 0.2M, the particle size again decreased due to inhibition of
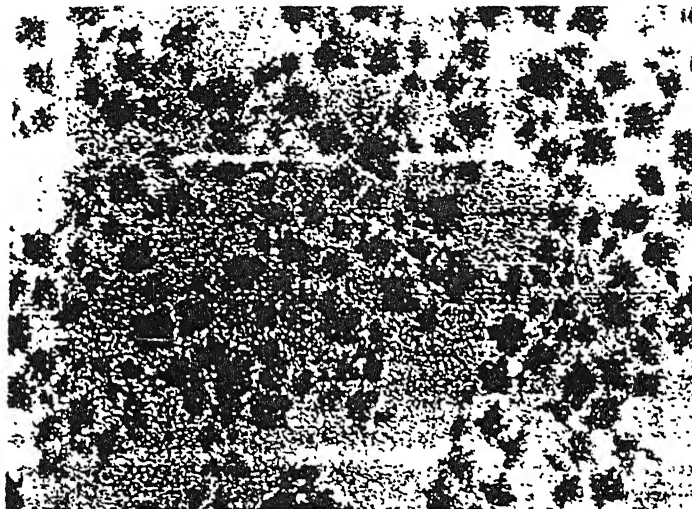
Fig 1.2.2 Nanosized monoclinic zirconia particles with narrow size distribution produced from forced hydrolysis of aqueous solution of zirconyl chloride salt (0.075M). [ref 1]
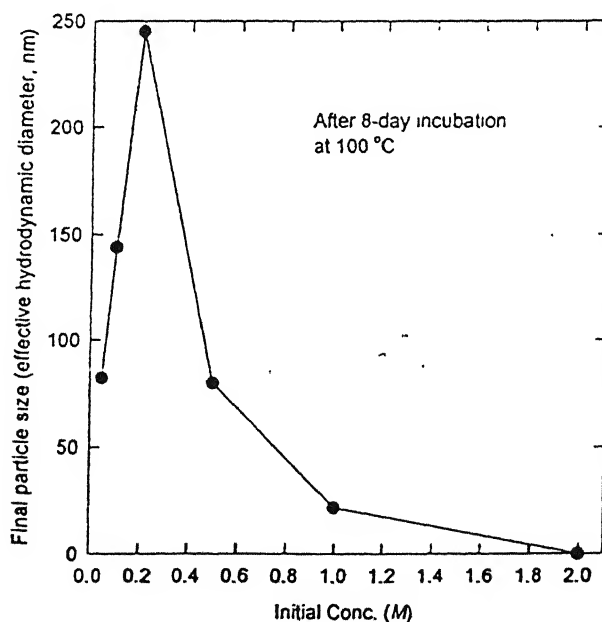
Fig 1.2.3 Influence of initial ZrOCl$_2$ salt concentration on the size of final colloidal sol particles. [ref 1]

reaction kinetics because of high acidity. Fig 1.2.3 shows the influence of initial ZrOCl$_2$ concentration (M) on the size of final colloidal sol particles.

In another recent work Matsui. K and Ohgai. M[10] have investigated the effects of H$^+$ and Cl$^-$ ion concentration on the secondary particle size of hydrous zirconia. The hydrolysis reaction can be expressed as follows:

$$ZrOCl_2 + (n+1) H_2O \longrightarrow ZrO_2.nH_2O + 2H^+ + 2Cl^-$$
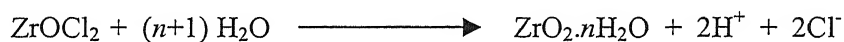
Hydrous-zirconia sol was synthesized by boiling aqueous ZrOCl$_2$ solution at 100^{0}C for 70-220 hour in a flask with a reflux condenser. ZrOCl$_2$ aqueous solutions with different H$^+$ and Cl$^-$ ion concentration were prepared by adjusting HCl addition to study this effect. These authors have obtained dependence of secondary particle size of hydrous zirconia on ZrOCl$_2$ concentration to be similar to that have already obtained by Hu. et. al.[1]. However, the crystal structure of hydrous zirconia prepared at 0.02 to 0.4 mol.dm^{-3} concentration was monoclinic, that differed from the crystal structure obtained at 0.5M.

The authors have found that when H$^+$ and Cl$^-$ ion concentration are controlled properly, then the average secondary particle size of hydrous zirconia increases as the H$^+$ ion concentration increases, reaching a maximum value of 200 nm when H$^+$ ion concentration becomes 0.44 mol.dm^{-3}. This can be explained by taking two factors into account, i.e. size and electric repulsion force factor. The primary particle size decreases with increase in H$^+$ ion concentration that causes an increase in surface energy of the primary particles. This eventually causes more aggregation among the primary particles and leads to increase of the secondary particle size with increase in H$^+$ ion concentration. But after reaching a critical concentration of H$^+$ ion (0.44 mol.dm^{-3}), electric double layer repulsion hinders aggregation among the

primary particles and causes decrease in the secondary particle size with further increase in H^+ ion concentration.

1.2.3.2 Kinetic processes in precipitation

The precipitation process consists of two distinct regions, nucleation and growth period. These regions are basically controlled by the supersaturation ratio (S*). When this supersaturation ratio (S*) exceeds the critical value, then nucleation occurs. But growth can occur at supersaturation ratios considerably lower than S* (Fig 1.2.4). To prepare monodisperse powders, the nucleation process must occur before the growth regime and in a shorter time period. But when the nucleation rate control period is long, then particles nucleated early grow to sizes that are considerably larger than those of the nuclei produced later in this rate-controlled period. This explains formation of polydisperse powders[11].

The duration of the nucleation period also determines maximum particle density that can be achieved. Uniform depletion of supersaturated species coupled with uniform growth condition for nuclei results in uniform particle density throughout the reaction medium.

1.2.3.3 Precipitation by using a base

Raising the pH of the solution can accelerate the hydrolysis reaction and this can be done rapidly by addition of strong bases like NH_4OH or slowly by addition of urea and subsequently heating the mixture. Hydrolysis by ammonia leads to the instantaneous formation of white precipitate that is difficult to control. But when urea is used for hydrolysis reaction, the pH of the solution increases
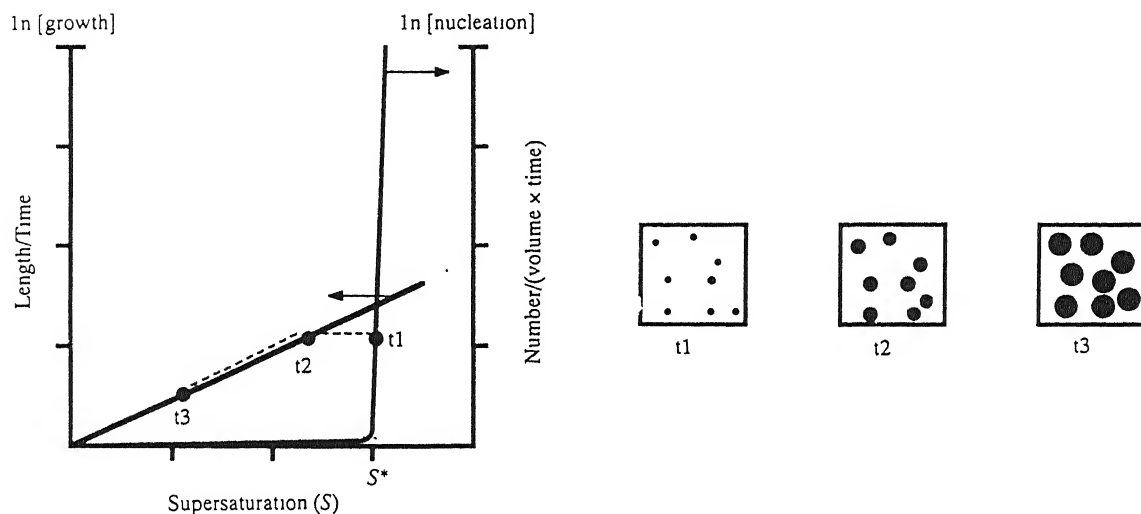
Fig 1.2.4 The separate regimes of nucleation (t1) and growth (t2, t3) rate control and their role in controlled precipitation of ceramic powders. (S = a/a$_0$, where a = activity of supersaturated species i in metastable solution and a$_0$ = activity of species i in solution equilibrated with an infinitely flat crystal). [ref 11]

slowly by a two-step hydrolysis of urea producing NH_3 and CO_2. In this case the process can be controlled more easily.

Huang Yue-xiang and Guo Cun-ji[12] have studied urea hydrolysis method by dissolving $ZrOCl_2.8H_2O$ (with various concentrations) and urea $[CO(NH_2)_2]$ into distilled water and then boiled continuously for 50 hours in a closed system that resulted in the formation of colloidal sol. The authors have proposed existence of classical crystal nucleation-growth process during boiling as indicated by Fig 1.2.5, which shows that with increase in boiling time particulate hydrolysis products formed and grew gradually to square shaped zirconia particles. It is well known that zirconyl ions are present as $[Zr_4(OH)_8.16H_2O]^{8+}$ tetramers in aqueous solution. During urea hydrolysis, when zirconyl chloride octahydrate is dissolved into
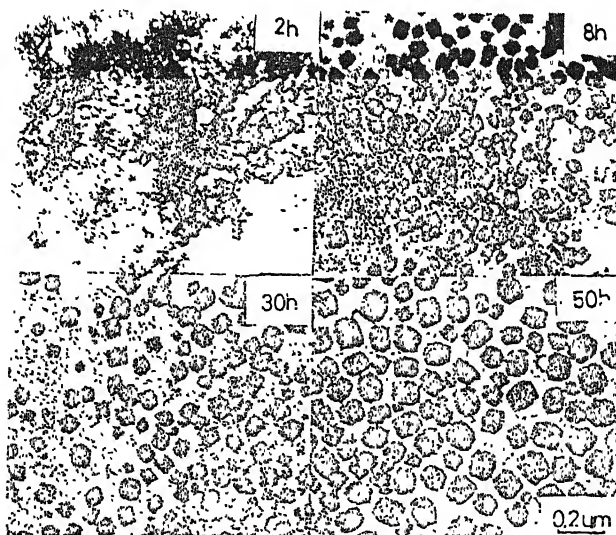
Fig 1.2.5 TEM micrographs of the hydrolysis products. The samples were extracted from 0.2 mol l^{-1} ZrOCl$_2$ solution at each definite boiling time [ref 12]
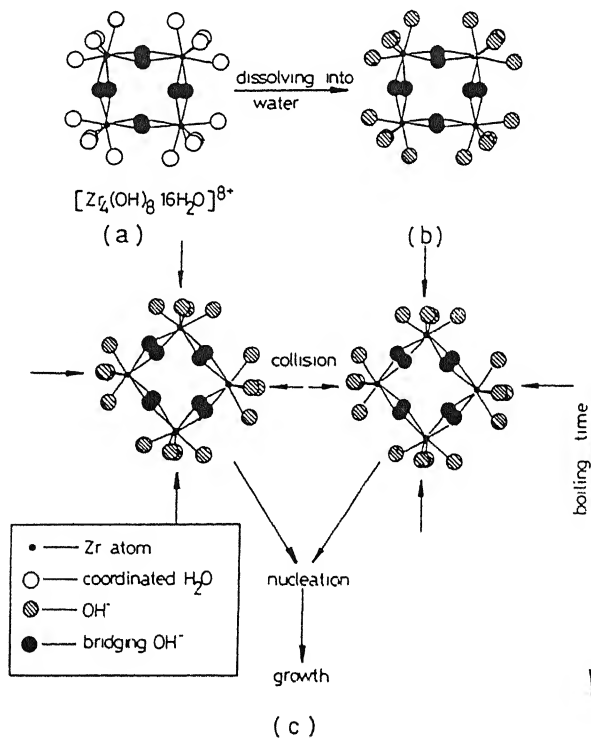
Fig 1.2.6 Proposed mechanism for hydrolysis product formation [ref 12]

water, the four coordinated water molecules are replaced by hydroxyl ions (Fig 1.2.6) obtained from the decomposition of urea according to the following reaction:

$$CO(NH_2)_2 + 3H_2O \longrightarrow CO_2 + 2NH_4^+ + 2OH^-$$
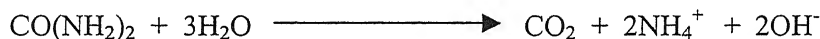
Condensation between the hydroxyl ions coordinated groups produce 'fluffy' crystal nuclei, which grow with boiling time to form monoclinic phase. During urea hydrolysis, the pH of the solution decreases at the initial stage due to $ZrOCl_2$ hydrolysis, which is followed by urea decomposition that leads to increase in pH of the solution. At longer boiling time period pH value becomes nearly constant due to equilibrium of these two chemical reactions. The agglomeration of the hydrolysis products was proposed to depend on the pH of the solution, i.e. amount of OH^- present. Higher the pH faster is the agglomeration.

They have also studied dependence of particle size of as-prepared hydrous zirconia on the initial concentration of $ZrOCl_2$ and obtained lowest mean particle size of 15 nm at $ZrOCl_2$ concentartion of 0.05 mol l^{-1} and boiling time of 50 hours.

In another work, Wang et.al.[6] have investigated precipitation method involving use of NH_4OH by taking aqueous solution of zirconyl chloride that was added dropwise into a vessel containing water and stirred and simultaneously 0.1M of NH_3 solution was added dropwise till pH became ~10. This alkaline solution was continuously stirred for 1 hour followed by aging for 24 hour till a precipitate formed that was washed with distilled water. The precipitate was dried at 120^0C for 4 hours followed by calcination at 400, 600 and 800^0C for 4 hours in air. They have reported nanocrystalline zirconia of average crystallite size less than 18 nm by calcination at 800^0C. This result showed that thermal-resistant nanocrystalline zirconia can be produced by precipitation method at a low cost.

1.2.3.4 Homogeneous precipitation by heating alcohol-water solution

All the precipitation processes discussed are associated with some drawbacks, mainly that they yield an agglomerated product with wide size distribution. Furthermore, many of them are very slow. In a recent work Moon et. al.[13] investigated a novel method that yielded spherical ZrO_2 precursor powders of narrow size distribution through microwave heating of zirconyl chloride solution with an alcohol-water mixture as the solvent. As the temperature of the starting solution increased, precipitation occurred because of the decrease of solubility due to the decrease of the dielectric constant. The kind and composition of the solvent mixture greatly influenced the behavior of the precipitation and the morphology of the resulting particles as both zeta potential and dielectric constant affect the electrostatic repulsion force between the particles. The authors have shown that spherical particles with narrow size distribution could be obtained by incorporating 1-propanol and 2-propanol as the alcohol in the solvent mixture. They have also studied the variation of dielectric constant and precipitation temperature with volume ratio of 2-propanol to water (R/H) and the result is shown in Fig 1.2.7. It can be seen from the figure that although the precipitation temperature decreases with R/H ratio, the dielectric constant at precipitation temperature is nearly constant. The authors have also found that particle size and particle agglomeration level could be controlled by amount of the surfactant (hydroxypropyl cellulose, HPC) in the solution. Variation of mean particle size and geometric standard deviation with HPC concentration is shown in Fig 1.2.8. At HPC concentration of $3X10^{-3}$ gm/cc, R/H 5, salt concentration 0.2 M, the mean particle size was 0.2 μ and standard deviation was 1.20.

In another work Moon et. al.[14] have reported that the morphology, size and size distribution of ZrO_2 particles were highly sensitive to the heating method
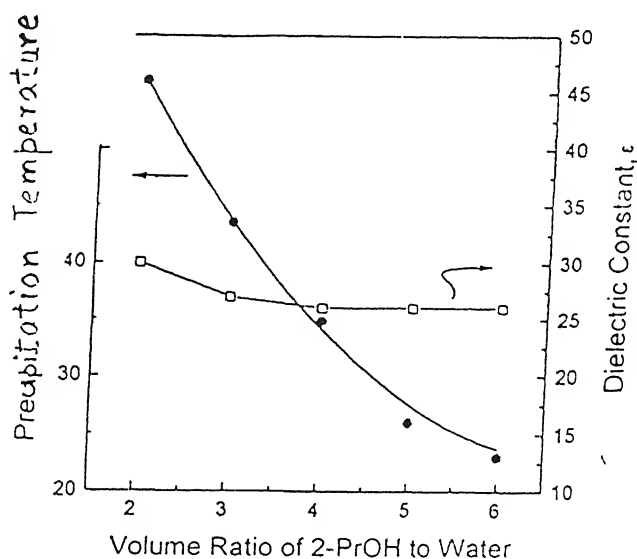
Fig 1.2.7 Variation of precipitation temperature and dielectric constant at precipitation temperature with volume ratio of 2-PrOH to water. The concentration of zirconyl chloride was 0.2 M [ref 13].
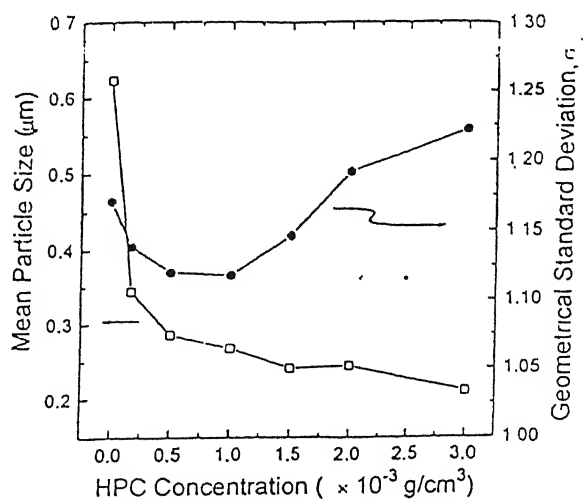
Fig 1.2.8 Variation of mean particle size and geometrical standard deviation with HPC concentration. The volume ratio of 2-PrOH to water and the concentration of zirconyl chloride were 5 and 0.2M respectively [ref 13].

used for the starting solution. The authors showed that particles produced under conventional heating methods were polydisperse, agglomerated spherical, or irregularly shaped because of inhomogeneous precipitation through the temperature gradient, shear force due to stirring, compositional nonuniformity and the low heating rate. When uniform and rapid heating was achieved by using microwaves then the precipitation occurred simultaneously throughout the solution and heterogeneous nucleation at the container wall was suppressed.

Jean and Ring[15] studied the effect of sterically stabilizing surfactants during synthesis of unagglomerated, monosized ceramic powders in order to give dense and uniform green compacts. TiO_2 powder was synthesized by hydrolysis of titanium ethoxide in alcohol solution in presence of HPC. The authors proposed two unique properties that any sterically stabilizing dispersants must have. Firstly, the dispersant must allow polymeric reaction products to diffuse through the adsorbed layer. Secondly, the dispersant must not be incorporated into the structure of the growing particles, i.e. it must be physically adsorbed and not chemically binding to the surface. They also showed that reaction yield decreased from 68.1% to 58.3% and particle number density increased from 5.5×10^{10} to 9.2×10^{10} per cc when HPC concentration was increased from zero to 1.71×10^{-3} gm/cc. The HPC molecules do not act as a heterogeneous nucleation sites and prevent agglomeration during growth even when higher reactant concentration is used.

In a recent study, Jindal[16] have prepared monodispersed nanoparticles of hydrous ZrO_2, ZrO_2-Y_2O_3 and ZrO_2-Gd_2O_3 by using the same method as Moon et. al.[13]. The author has studied the influence of various factors such as concentration of the salt, rate of heating and heating time on size and morphology of the particles and found that for 0.1M, 0.05M and 0.01M $ZrOCl_2$ concentration,

nearly spherical, monodispersed particles of sizes 305 nm, 200 nm and 144 nm respectively are produced when no dispersant is used. The particle size decreases by a factor of 4 (i.e. from 430 nm to 100 nm) when the heating time is decreased from 60 s to 10 s. Effect of dispersants was also investigated by adding small amounts of sodium hexametaphosphate (SHMP), acetylacetone (AcAc). Addition of AcAc decreased the particle size significantly from 350 nm to 150 nm when 1ml AcAc was added to a 0.1M $ZrOCl_2$ solution. Higher concentration of AcAc completely suppressed the precipitation of particles. The amorphous powders were crystallized by hydrothermal treatment without any increase in the particle size that confirms topotactic crystallization.

1.2.3.5 Role of washing in the preparation of nano particles

A major step in powder preparation is the washing of the powder after precipitation. The purpose is to remove chlorine by washing with water or to reduce hard agglomerates by washing with alcohol. Chlorine is known to hinder the sintering and densification of zirconia powders and enhances particle coarsening by Oswald ripening [17].

When powders are washed with water then bridging among the particles occurs by hydrogen bonding of water to two terminal hydroxyl groups. But with the drying process these bridging water molecules are gradually lost, but till close proximity among the particles causes hydrogen bonding between terminal hydroxyl groups of the different particles. Therefore further dehydration leads to the formation of actual chemical bonds (reaction shown below) preferentially between the particles that cause hard agglomerates.

$$Zr\text{-}OH \ + \ HO\text{-}Zr \quad \longrightarrow \quad Zr\text{-}O\text{-}Zr \ + \ H_2O$$
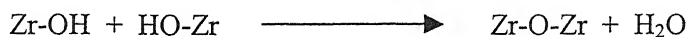
Kaliszewski and Heuer[18] reported the formation of surface ethoxy groups from FTIR spectroscopy, when the powders are washed with ethanol. These surface ethoxy groups effectively hindered the closet approach between the particles and consequently prevented the formation of Zr-O-Zr bonds and therefore hard agglomerates do not form.

1.3 NANOPARTICLES: PARTICLE SIZE MEASUREMENT BY DYNAMIC LIGHT SCATTERING (DLS)

The particle size of nanosized zirconia can be measured by various techniques, such as transmission electron microscopy or dynamic light scattering. In the present study transmission electron microscopy as well as dynamic light scattering technique have been used. The later is described in the following section.

1.3.1 Principles of Dynamic Light Scattering

Scattering intensity fluctuations are the basis of dynamic light scattering. If the particles suspended in a fluid medium are illuminated by a light source such as a laser, the particle will scatter light in all directions. The intensity of the scattered light will fluctuate with time due to Brownian motion. An important feature of Brownian motion for DLS is that smaller particles move quickly and larger particles move more slowly. The fluctuations in the scattered light intensity are used to obtain diffusion coefficient (D) of the particles suspended in the fluid medium. If refractive index and viscosity of the suspending fluid medium are known, then mean

particle size (also known as Z-average size) can be derived from measured diffusion co-efficient of particles.

Time dependent auto-correlation functions provide a concise method for expressing the degree to which two dynamical properties are correlated over a period of time[19]. The DLS technique basically measures this time dependent auto-correlation function c(q, τ), defined as

$$c(q,\tau) = \frac{<I_s(q,t).I_s(q,t+\tau)>}{<I_s(q,\tau)>}$$

Where I_S (q, t) is scattered intensity at time 't' and I_S (q, t + τ) at a time (t + τ). The quantity q is the difference between the incident wave vector q_i and the scattered wave vector q_s. The angular bracket denotes average of the included quantity.

The auto-correlation function depends on the correlation time in case of suspension containing monodispersed particles through the equation[20]

$$C'(\tau) = A\big[1 + b\exp\big(-2Dq^2\tau\big)\big]$$

$$\text{or, } \left[\frac{C'(\tau)}{A} - 1\right] = C(\tau) = b\exp\big(-2Dq^2\tau\big)$$

Where, A = Background intensity

   b = Experimental constant

   D = Diffusivity of the particle

A plot of $\ln c(\tau)$ vs. τ gives a straight line with slope of $-2Dq^2$. Therefore effective particle radius 'r' can be obtained from Stokes-Einstein equation.

$$D = \frac{kT}{6\pi\eta r} \tag{1.3.1}$$

Where η = Viscosity of suspending medium

k = Boltzman's constant

T = Temperature

If the intensity signal from any point of a particle at time 't' is to be compared to the intensity signal after a very short time later (t + δt) – then it is seen that these two signals are strongly correlated. If again the original signal is compared with little further ahead of time, i.e. (t + 2δt), then there still be a relatively good comparison between the two signals; but it will not be as good as (t + δt). In this way, these two signals will have no relation with each other if the time interval for comparison is comparatively large as due to random motion (i.e. Brownian motion). In case of a sample containing particles of different size classes, the correlation function consists of weighted sum of exponentials, each with a different delay constant. Therefore ln c(τ) vs τ plot would give rise to a curved line, with ln c(τ) gradually decreasing as t ⟶ ∞ .

In this case, the auto-correlation function can be expressed as a sum of exponentials

$$C'(\tau) = A\left[1+b\left\{\sum_i L_i \exp(-D_i q^2 \tau)\right\}^2\right]$$

so that

$$\frac{1}{b}\left[\frac{C'(\tau)}{A}-1\right] = C(\tau) = \left[\sum_i L_i \exp(-\Gamma_i \tau)\right]^2 \qquad (1.3.2)$$

where, $\Gamma_i = D_i q^2$

If particle size distribution is assumed to be continuous, then this sum can be replaced by an integral

$$C(\tau) = \left[\int\limits_{0}^{\infty} G(\varGamma) exp(-\varGamma\tau) d\varGamma \right]^2 \qquad (1.3.3)$$

To obtain a reasonable fit by using equation (1.3.2), it is written as

$$C(\tau) = \left[\sum_l L_l \exp\left(-\frac{\tau}{t_i} \right) \right]^2$$

where , $t_i = \dfrac{1}{\varGamma i} = \dfrac{1}{D_i q^2}$

Now, 't_i' is obtained from least square fit. The mean relaxation time is given by

$$t_m = \sum_l a_i t_i$$

where $a_i = \dfrac{L_i}{\sum L_i}$

and, the mean diffusion coefficient or mean diffusivity is

$$D_m = \frac{1}{t_m q^2} \qquad (1.3.4)$$

by using Stokes-Einstein equation given in Eq (1.3.1), mean particle size is obtained by using mean diffusivity given in Eq (1.3.4).

1.3.2 Dynamic light scattering (DLS) System

In the present study the instrument that uses dynamic light scattering technique is called High Performance particle Sizer (HPPS, model number *HPP5001*) supplied by Malvern Instruments Ltd., UK.

This system [21] comprises of six main components (fig.1.3.1). In the system a laser (i) (He-Ne, 30mW, 633mm) is used to provide source of light for illumination of the particles within the sample. The sample is placed within the
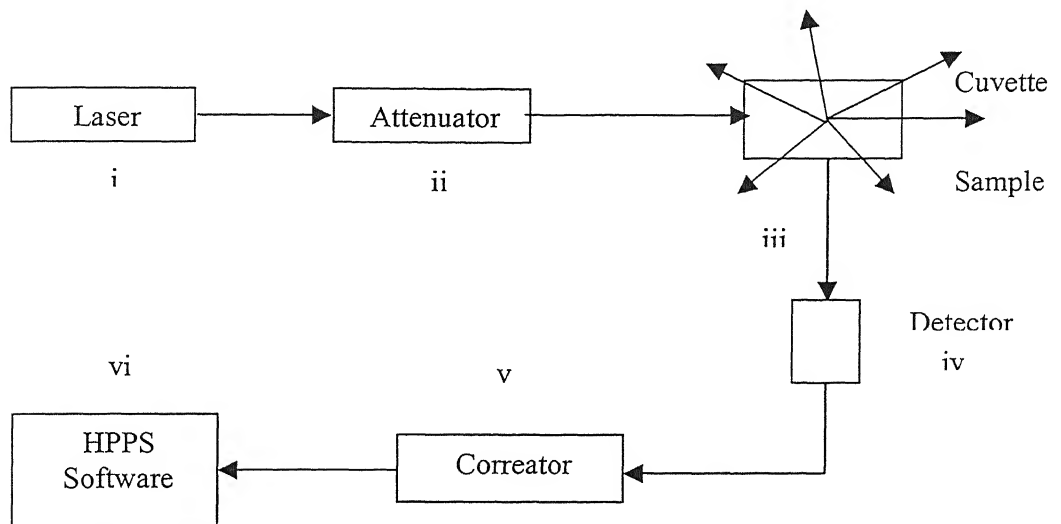
Fig: 1.3.1 Schematic of a dynamic light scattering arrangement

cuvette (iii). Most of the laser beam passes unscattered through the sample, but some

but some is scattered by the sample particles. A detector (iv) is used to measure the

intensity of the scattered light. In most DLS system, a detector is positioned at 90^0 to

the laser, although it is possible to place the detector in any positioned and because

particles scatter light in every directions.

The HPPS system (supplied by Malvern Instrument)

basically measures the scattering information close to 180^0, which is known as

"Backscatter detection" (fig 1.3.2).
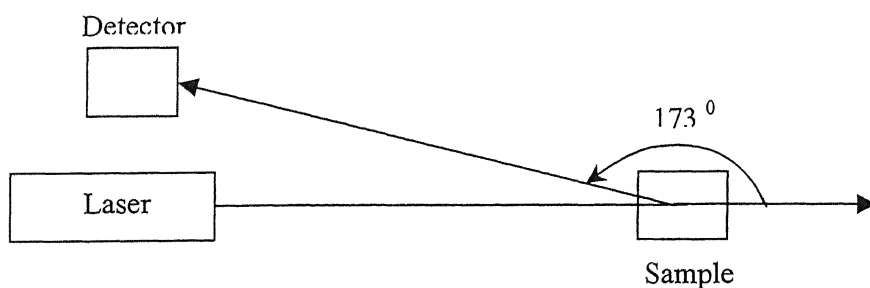
Fig 1.3.2 Backscatter geometry in HPPS

Due to back scattering measurement, the laser need not travel through the entire sample. This reduces *multiple scattering effects*, where scattered light from one particle is itself scattered by other particles. As the light passes through a shorter path length of the samples, then higher concentrations of samples can be measured. Also larger particles such as dust within the dispersant mainly scatter in the forward direction. Therefore by measuring the backscatter, effect of dusts is greatly reduced. Another unique feature with which HPPS system is equipped in that the cuvette position changes during measurement. For samples of higher concentration or larger particles, measuring closer to the curette wall will reduce multiple scattering effects. Conversely, for samples of lower concentration, movement of measuring point away from the cuvette wall, i.e. towards the center of cuvette would be beneficial to maximize the amount of scattering from the sample.

The intensity of the scattered light must be within in a specific range for successful operation of the detector. If too much light is detected, then the detector will become overloaded. To solve this problem, an attenuator (ii) is used in order to reduce the intensity of the laser and subsequently reduce the intensity of the scattering. The samples that contain very small particles or low concentration do not scatter much light. So, in this case, the amount of scattered light must be increased. In this situation, the attenuator will allow more laser light through the sample. But in case of concentrated samples, the attenuator will allow less laser light to pass through the sample. The scattering intensity signal for the detector is passed to a signal processor called correlator (v). The correlator compares the scattering intensity at successive time intervals to derive the rate of decay of the intensity signal. The correlator information is then passed to HPPS software (vi), which will analyze the data and derive size informations.

1.4 STATETMENT OF THE PROBLEM

As was discussed in the earlier sections, the preparation of monodispersed, nanosized hydrous zirconia particles by homogeneous precipitation method is attractive compared to other chemical routes like forced hydrolysis, hydrolysis using a base etc. due to its certain advantages like shorter preparation time, narrow distribution etc. Use of an organic solvent in aqueous solution containing metal salt reduces the dielectric constant of the mixture and heating of that mixture further decreases dielectric constant. As a result solubility of the salt decreases and eventually causes precipitation.

In the present study, to obtain monodispersed, nano sized ZrO_2 particles, heating of alcohol-water solution containing zirconyl chloride salt is proposed to be investigated. Microwave treatment to ensure uniform heating throughout the solution is planned to be carried out. Study of the effect of zirconyl chloride concentrations on particle size and morphology of hydrous ZrO_2 is proposed to be investigated. Furthermore, to control the particle size and agglomeration level, use of a surfactant, hydroxypropyl cellulose (HPC), with different concentrations is also proposed to be studied. The crystallization behavior of the as prepared zirconia powders is planned to be studied.

The particle size of the prepared powders is proposed to be measured by transmission electron microscope (TEM) as well as by an instrument (HPPS) based on dynamic light scattering. As the instrument was newly acquired, its calibration and application is to form essential part of the work.

CHAPTER 2

EXPERIMENTAL

The main aim of the present work was to prepare nanosized powders of zirconia by homogeneous precipitation. To measure the particle size, an instrument based on dynamic light scattering, namely High Performance Particle Sizer (HPPS) supplied by Malvern, UK was used in addition to the transmission electron microscope. Another main objective of the present work was to calibrate this instrument and gain confidence in its results. For this purpose, samples of known size were first measured using HPPS. Secondly, the zirconia particles prepared by homogeneous precipitation were characterized using TEM and HPPS and the results were compared. In the following, the procedures for the preparation of standard samples for measurement, preparation of zirconia particles and their measurement and for further characterization of the prepared powders are discussed.

2.1 PREPARATION OF SAMPLES FOR CALIBRATION OF THE INSTRUMENT HPPS

Particle size of some commercially available nearly monosized ceramic powders was measured using HPPS. The following powders were used for this purpose:

1. Standard latex sample (Duke Scientific Corporation, supplied by Malvern Instruments, U.K).

2. Sumitomo alumina (supplied by Sumitomo Chemicals Co. Ltd, high purity alumina, Type AKP-50), nominal particle size 0.2 μm.

3. Zirconia (supplied by TOSOH, Japan), nominal size 0.2 μm.

4. Particles of zirconia prepared in the laboratory (as prepared and also subjected to various treatments).

In the following section the details of preparation of the above-mentioned samples are described.

2.1.1 Preparation of Standard Latex Sample

100 ml of distilled water was taken and filtered through 0.22 μm filter paper. Then 0.05844 gm of sodium chloride was added to distilled water in order to prepare 10 mM of sodium chloride solution. Then the solution was stirred well so that NaCl was fully dissolved. Then one drop of latex sample was added to this solution and shaken well so that it was fully dispersed. Similarly latex standard spheres with filtered distilled water medium was also prepared by adding one drop of it into 100 ml of distilled water and subsequently shake it well.

2.1.2 Preparation of Alumina Suspensions

Suspension of alumina of 0.001, 0.005, 0.1 and 1-volume percent were prepared. For these 0.0009, 0.0049, 0.0997 and 0.9975 gm respectively of alumina were weighed and stirred in 25 ml of pH 3 solutions separately. Then these suspensions were subjected to stirring followed by ultrasonication so that alumina powders were in well-dispersed condition. Then these suspensions were allowed to settle for the calculated time period. After that the particle size was measured.

2.1.3 Preparation of TOSOH-ZrO₂ Suspensions

0.005, 0.01, 0.02 and 0.03 volume percent suspensions of TOSOH-ZrO_2 were prepared by dissolving 0.009, 0.018, 0.036 and 0.054 gm of powder in 30 ml of distilled water (filtered through 0.22 μm filter paper) containing hydroxy propyl cellulose in two concentration of $2.5X10^{-3}$ gm/ml and $1X10^{-3}$ gm/ml. The suspensions were stirred and ultrasonically agitated to break the agglomerates. Finally, these suspensions were allowed to settle by gravity. After the different time periods, few ml of these suspensions were taken out from top 10 mm of the respective suspensions by a pipette. Then particle size was measured by HPPS.

2.2   PREPARATION OF ZIRCONIA POWDERS

2.2.1 Standard method for preparation of zirconia powders

The starting materials used for preparation of ziconia powders in the laboratory are given in Table 2.1.1. All reagents and solvents were used in the as-received form, with no further purification.

Table 2.2.1. Starting materials for synthesis of zirconia powder in the laboratory

Materials	Molecular weight	Source	Assay
Zirconyl Chloride Octahydrate ($ZrOCl_2.8H_2O$)	322.25	C.S Zircon Products, India	99.5%
Iso Propyl Alcohol (C_3H_7OH)	60.10	NICE, India	99%
Dispersant: Hydroxypropyl cellulose (HPC)	80,000	Aldrich Chemical Company Inc	-
Ammonia Solution (25% NH_3)	17.024	NICE, India	99.9%

The flowchart of the process used here is shown in Fig 2.2.1.

```
┌─────────────────────────────┐        ┌─────────────────────────────────┐
│  ZrOCl₂ aqueous solution    │        │  Isopropyl alcohol + surfactant │
│                             │        │        Cooled to 3⁰ C           │
└─────────────────────────────┘        └─────────────────────────────────┘
                              │        │
                              └────┬───┘
                                   ▼
                        ┌─────────────────────┐
                        │   Stir, cool to 3⁰ C │
                        └─────────────────────┘
                                   ▼
                     ┌─────────────────────────────┐
                     │ Precipitation by microwave   │
                     │          heating             │
                     └─────────────────────────────┘
                                   ▼
                     ┌─────────────────────────────┐
                     │  Add NH₄OH to bring pH ~7    │
                     └─────────────────────────────┘
                                   │        d < 100 nm    ┌──────────────────┐
                                   ├─────────────────────▶│  Characterization │
                                   │        d > 100 nm    └──────────────────┘
                                   ▼
                     ┌─────────────────────────────┐
                     │  Centrifuge at 10000 rpm,    │◀───────┐
                     │          45 minutes          │        │
                     └─────────────────────────────┘        │
                                   ▼                         │
                     ┌─────────────────────────────┐        │
                     │   Wash with DI water by      │────────┘
                     │  stirring well for one hour, │
                     │          6-7 times           │
                     └─────────────────────────────┘
                                   ▼
                     ┌─────────────────────────────────┐
                     │ Wash with alcohol and again      │
                     │          centrifuge              │
                     └─────────────────────────────────┘
                                   ▼
                     ┌─────────────────────────────────┐
                     │ Drying at 80⁰ C and Characterization │
                     └─────────────────────────────────┘
```

The flowchart boxes contain the following text:

- $ZrOCl_2$ aqueous solution
- Isopropyl alcohol + surfactant Cooled to 3^0 C
- Stir, cool to 3^0 C
- Precipitation by microwave heating
- Add NH_4OH to bring pH ~7
- d < 100 nm → Characterization
- d > 100 nm
- Centrifuge at 10000 rpm, 45 minutes
- Wash with DI water by stirring well for one hour, 6-7 times
- Wash with alcohol and again centrifuge
- Drying at 80^0 C and Characterization

Fig 2.2.1. Flow chart of experimental procedure

The apparatus used for heating was an ordinary kitchen microwave (2450MHz, 1350W$\pm$10%, BPL, India). The microwave could operate at 0-100% of full power. A refrigerator (LEONARD, Model No. 126A106174, Capacity 165 liter) was used for cooling of the solution.

The concentration of zirconyl chloride was varied from 0.005M to 0.1M and the volume ratio of iso propyl alcohol to water in the starting solution was 5. The dispersant used was hydroxypropyl cellulose (HPC). The concentration of HPC was also varied from 1.875 to 62.50 micromolar to study the effect of dispersant on particle size and morphology. The volume of the salt solution was either 5 ml or 10 ml and the corresponding isopropanol volume was 25 ml or 50 ml. The amounts of the various ingredients actually taken are given in Table 2.2.2.

Required volume of isopropyl alcohol was taken and required amount of dispersant (HPC) was added to it and stirred well so that HPC was fully dissolved in the solvent. This solution was cooled to 3^0 C in the refrigerator (first some ice cubes are taken in a plastic tray and the beaker containing the solution was put into the ice cube, then the plastic tray containing the beaker was kept inside the refrigerator). Zirconyl chloride aqueous solution was added to this precooled isopropyl alcohol and stirred well. This starting solution was again cooled at 3^0 C. The solution was then taken out quickly from the refrigerator and was heated in the microwave oven for 20 s at and 80% power.

When the starting solution was heated, it became supersaturated and precipitated shortly since solubility of the salt decreases with increase in the temperature. To avoid shear-induced agglomeration the starting solution was uniformly heated in the microwave chamber without stirring. Precipitation was continuous up to approximately the boiling temperature of the starting solution that is

around 80^0 C. Just after taking out the solution from the microwave the pH was ~1.30 - 2.80. After precipitation, the mother liquor was neutralized by adding 3-4 ml (approximately) of 1:1 NH_4OH solution to attain a pH between 6.5 to 7.5. This neutralization prevented the precipitates from redissolving.

Table 2.2.2 Actual weight of the different ingredients taken during synthesis of hydrous zirconia

Sl No.	$ZrOCl_2.8H_2O$		Alcohol (ml)	Water (ml)	Dispersant (1.7×10^{-3} gm/cc)
	Molar Conc.	Wt in grams			
1.		0.1026	25	5	0.0525
	0.01				
2.		0.1946	50	10	0.1026

2.2.2 Washing and drying of as prepared hydrous zirconia powders

The precipitates were washed with lukewarm deionized water by stirring for approximately 1 hour and then centrifuged repeatedly at ~ 10000 rpm for 45 minutes. The steps were repeated until there were no chlorine ions detected in supernatant solution with N/50 silver nitrate solution. Very thick white precipitate appeared on addition of silver nitrate solution after first washing but the amount of the precipitate decreased as the number of washings increased. Generally 7 washings were enough to remove chlorine ion by using lukewarm water. It was observed that pH of the solution decreased to ~ 4- 4.5 after each centrifuging which caused the precipitate to dissolve back into the solution. So after each centrifuging, the pH was increased to 7.5- 8.0 by addition of 1:1 NH_4OH solution to prevent redissolving of the precipitate. In Table 2.2.3 measured pH after every centrifuging in case of 0.05 M $ZrOCl_2.8H_2O$ solution is described in details.

The water washed precipitates were then washed with propanol by stirring for ~2 hours and again centrifuging at ~10000 rpm for 30 minutes to remove propanol. The propanol washed precipitate was again suspended in fresh propanol. The washed sample was then dried at 90^0C in an oven for around 1.5 - 2 hours. It was found that centrifuging at very high speed (10000 rpm) was not able to separate hydrous zirconia precipitate from nanosuspension of concentration below 0.05 M. In the present study centrifuging was carried out only for 0.05 and 0.1 M samples.

Table 2.2.3 Measured pH during centrifuging of 0.05 M ZrOCl$_2$.8H$_2$O suspension

Centrifuging cycle no.	pH after centrifuging	pH after 1:1 NH$_4$OH addition
1.	4.35	7.30
2.	5.60	7.55
3.	6.00	7.20
4.	7.52	8.00
5.	7.63	No NH$_4$OH addition
6.	7.62	No NH$_4$OH addition
7.	7.00	No NH$_4$OH addition

2.2.3 Crystallization of washed, dried powder

The hydrous zirconia powder synthesized by microwave was amorphous in nature. So it was made into crystalline form either by hydrothermal or calcination technique.

Hydrothermal Crystallization: It was carried out by using a pressure vessel (Parr Acid Digestion Bomb, ref. Table 2.2.4) at a temperature of 230^0C, 6 hours. In the present study, only 10 ml of the alcohol-water suspension was taken within the bomb. Since vapor pressure table for alcohol-water mixture in a ratio of 5:1

is not available, therefore it was not possible to find out the pressure generated within the pressure vessel at the corresponding temperature. After the hydrothermal treatment, the cover of the pressure vessel was opened and the contents were removed and the vessel was cleaned carefully.

Calcination: For calcination the required amount of powder was taken in a ceramic boat and heated at 200^0, 400^0 and 600^0 C respectively for one hour and 600^0 C for six hours.

Table 2.2.4 Specification of Parr Acid Digestion Bomb

Bomb part number	Size, mL	Maximum charge, grams		Recommended maximum temperature (^{0}C)	Absolute maximum temperature (^{0}C)	Absolute maximum pressure (psig)
		Inorganic sample	Organic sample			
4744	45	2.0	0.2	250	250	1800

2.2.4 Sample preparation for particle size measurement of particles in mother liquor by HPPS

One of the main precautions for measurement by HPPS is that the sample should not be settled during entire measurement or in other words it should be well dispersed. Mother liquor of concentration below 0.05 M $ZrOCl_2.8H_2O$ is stable enough for measurement. But sample of concentration greater than 0.05 M $ZrOCl_2.8H_2O$ settle down fast (just after few minutes of preparation). So these need further treatment for HPPS measurement.

For this, first 12.5 micromolar ($1.0X10^{-3}$ gm/cc) of HPC was dissolved into propanol. Then few drops of the mother liquor (usually 35 drops) are added to this propanol-HPC solution (usually 15 ml). This suspension was stirred well

and subjected to ultrasonication for better dispersion. After that the sample was measured for particle size by HPPS.

2.2.5 Sample preparation for particle size measurement of dried and, or calcined powder by HPPS

Dried and, or calcined powders also need further treatment for better dispersion. For this purpose, a pinch of powder was added to 15 ml of propanol containing 12.5 micromolar (1.0×10^{-3} gm/cc) of HPC. Then the solution was stirred well and ultrasonicated to break the agglomerates. Then few drops of this suspension (usually 35 drops) were again added to 15 ml of propanol-HPC solution, and again stirred and ultrasonicated for better dispersion. After that the sample was ready for measurement by HPPS.

2.2.6 Sample preparation for study of dissolution kinetics of hydrous zirconia suspended in mother liquor

For this study, the beakers and cylinders used in the experiment were all washed with distilled water (filtered through 0.22 μm filter paper). Then starting solution was prepared by following the flow chart (fig 2.2.1). The starting solution was also filtered through 0.22 μm filter paper before microwave heating at 80% power and 20 seconds heating time. The pH of the hydrous zirconia precipitate was not increased, i.e. pH of the precipitate was as prepared (~1.90). Then particle size was measured by HPPS only at subsequent time interval to study dissolution kinetics of hydrous zirconia suspension.

2.3 <u>MEASUREMENT OF SIZE OF NANOPARTICLES</u>

The particle size of the prepared powders was measured by (i) high performance particle sizer and (ii) TEM. Procedures for these measurements are described below.

2.3.1   Measurements of particle size by HPPS

2.3.1.1   Using the instrument

As was discussed in the earlier chapter, High Performance Particle Sizer (HPPS) has been newly procured. HPPS gives the option of carrying out the measurement either in manual mode or by creating/modifying an SOP (Standard Operating Procedure). In the present study, manual measurement was performed by selecting 'Measure-Manual'. The measurement parameters dialogue (with three-tabs) appeared and allowed the operator to set all measurement options. These three tabs are *documentation, sample setup and measurement setup tab* respectively. The *documentation tab* gives the option of sample name and also comments on the sample. Temperature, solvent or dispersant properties (viscosity and refractive index) and sample property (refractive index for calculation of volume distribution) are fed in the *sample setup* tab. *Measurement setup* tab allows a control over accuracy and repeatability of the measurement quality by Normal, Enhanced and Custom settings. The difference between normal and enhanced setting is the time it takes to make a measurement. An enhanced quality measurement may take much longer time compared to normal quality measurement and will give more stable distributions. The custom setting can be used to manually define the number of runs and run duration. In the present study, it has been found that the HPPS run in the custom setting produced sporadic result.

The fundamental size distribution generated by DLS technique is an intensity distribution. The X-axis shows a distribution of size classes, while Y-axis shows relative intensity of the scattered light. The results section gives three informations i.e. Z-average size (also known as cumulants mean), polydispersity index and peak modes. The steps in the measurement by HPPS are given in Appendix-1.

2.3.1.2 Measurement of Refractive Index and Viscosity

As mentioned in section 2.3.1.1, HPPS requires some physical properties, viz. refractive index and viscosity of the solvent/dispersant used. Refractive index was measured by using REFRACTOMETER (INNCO, INDIA), which is capable of measuring refractive index in the range of 1.33 to 1.40. In the present study refractive index of solutions containing 0.001, 0.01, 0.03 and 0.1M $ZrOCl_2 8H_2O$ respectively were measured. Concentration of HPC was 1.7×10^{-3} gm/cc. These solutions were not subjected to microwave heating. It was found that, R.I of 0.001 and 0.01M solutions were 1.375 and 1.376 respectively. But R.I of 0.03 and 0.1M solutions was not possible to measure since it was out of the range of the instrument. So for particle size measurement by HPPS, suspensions containing zirconyl chloride and HPC, refractive index of value 1.376 was used in every case.

Viscosity of the suspensions was measured by using THE BROOKFIELD DIGITAL VISCOMETER (LV model). Table 2.3.1 shows a typical example for measurement of viscosity for a sample.

Table 2.3.1 Measurement of viscosity for zirconyl chloride suspension

Spindle number	Speed (rpm)	Sample details	Factor	Actual reading	Viscosity (cps)
18	12	0.01M, 1.7 H (3rd) pH=8.50	2.5	1.7	4.25
	30		1.0	4.6	4.60
	60		0.5	8.6	4.30

To convert viscometer dial reading to viscosity (in centipoises or mPa-s), the actual dial reading should be multiplied by the corresponding factor for corresponding speed. As for example from Table 2.3.1, it is observed that for 60 rpm speed viscometer dial reading is 8.6. So this reading must be multiplied by the corresponding factor i.e. by 0.5 and ultimately viscosity becomes 4.30 centipoise.

2.3.2 Measurement of particle size by Transmission Electron Microscope (TEM)

2.3.2.1 Preparation of formvar solution for coating of TEM grid

A 2% solution was made, by dissolving 2 gm of formvar powder (Ernest F. Fullam, Inc., NY) in 100 ml of chloroform and shaken slightly and then kept overnight so that the formvar dissolved fully. Then the solution was filtered through Wattman 41 filter paper to remove impurity materials. Initially 0.4, 0.5 and 1% solution were prepared, but these produced so thin film so that it was not possible to separate from the glass slide. Therefore 2% solution was considered to be the optimum concentration for producing of thin film. The film thickness also depends on other factors like speed with which formvar solution is taken out of the funnel. If the

speed of the formvar is high then it gives thick film, and if slow then it gives a thin film.

2.3.2.2 Procedure for coating of TEM grids

For coating of TEM grids following items were required

1. Copper grids, Type G400 (Polaron Equipment Ltd. Watford. England) with mesh size 300 (i.e. 300 parts per inch) and diameter 3.05 mm.

2. Poly vinyl formal, formvar (Ernest F. Fullam, Inc., NY).

3. Scalpel Blade with handle.

4. Fine pointed forceps (VIGOR, B.Jadow Inc., Switzerland).

5. Separating funnel with a stop cock (50 ml).

6. Distilled water.

7. Glass slides (Blue Star).

8. Petridish.

First glass slides were washed with vim powder and then with distilled water and finally rinsed with acetone. Then the slides were gently wiped by a tissue paper. To make sure that the slides were absolutely clean, the slides were seen against light and if there were any spots then those were removed with great care because the film sticks there and then it becomes extremely difficult to take out film from slide.

Stopcock of the separating funnel was closed first and then formvar solution was poured in the separating funnel in such a way so that almost half of glass slide could be immersed within formvar solution. Now the glass slide was put within formvar solution gently and the stopcock was opened. The speed at which formvar solution was drained can be changed according to the required thickness of film, but a

uniform speed should be maintained during withdrawal time. The slide was gradually taken out of the funnel after draining out of the whole solution. Normally there was some liquid remaining at the end of the slide. Now a formvar film adhered at both sides of the slide. If the film is too thick then it shows coloration. But if it is thin then it is difficult to make out as to how much area it is covering. This can be checked by blowing some air from mouth that makes the film visible.

The corners of the glass slide were scraped off with the help of scalpel blade. Then the front end of the slide (which was coated) was placed over the surface of distilled water in such a fashion so that it just touched the water surface. The other end of the slide (which was not coated) was gripped by hand. The angle at which slide was placed over water surface should be near to 180^0 i.e. the slide should be placed close to horizontal for smooth separation of the thin film. Then with the help of the blade the immersed end was separated out gently from the slide. Once one end of the film started to come out, then rest came slowly due to the force exerted by water. Once all of the film came out, it floated on water. Sometimes it was difficult to separate the last end of the film from the slide. So at this time it was wise to cut that end with great care so that the other part of the film was not damaged.

Then with the help of the forecep the grid was gently taken out (so that it should not be bent) from the grid box and was seen under table lamp which side was rough. The grid was then put on the film so that this rough side adhered to film for most secure adhesion of grid with the film. Another glass slide was taken and its' one end was gently put on one end of the film and quickly raised so that film also came on the slide along with the grid positioned in between film and slide. Care should be taken so that the contour of slide and film were in same position, otherwise wrinkle formed on the film surface. The coated grid was kept under a lampshade for

20 minutes, till water was dried. In this way, two grids could be coated simultaneously.

2.3.2.3 Sample preparation for mother liquor and dried, and or calcined powder for TEM analysis

The sample preparation for mother liquor and dried, and or calcined powder for measurement by HPPS has already described in section 2.2.4 and 2.2.5 respectively. Same method was followed for sample preparation for TEM analysis. After preparation small volume of the requisite sample was taken out with the help of a glass pipette. Then one drop of this suspension was added over the coated grid still sticking to the glass slide. Care was taken so that the tip of the pipette does not touch the grid, otherwise the fragile coating could break. It is to be noted that, for concentrated suspension one drop is enough, but for too dilute suspension more than one drop is necessary. The grid was again put under a lampshade for nearly 20 minutes so that it dried. The grid was then separated from the glass slide gently using scalpel blade. This grid was then ready for observation in TEM.

In the present study, for comparison of particle size by TEM and HPPS, addition of sample drop over the grid and HPPS measurement were done at the same time.

2.3.2.4 Measurement condition

The particle size and morphology were observed by using a Transmission Electron Microscope (JEOL FX 2000, Japan). The electron microscope was operated at 120 KV.

2.4 <u>X-RAY DIFFRACTION</u>

The phases present was determined by x-ray diffraction technique. XRD pattern of the powder sample was taken with a RICH. SEIFERT ISO-DEBYEFLEX2002 diffractometer using CuK_{α} (λ=1.54184Å) radiation with a monochromator. The powders of the requisite sample were packed on a glass slide to make the specimens and the surface of the powder was smoothened by pressing another glass slide over it. The powder was soaked with a few drops of methanol for most secure adhesion to the glass slide.

The x-ray diffraction plot of the samples was taken between $2\theta = 20^0$ and $2\theta = 80^0$. The conditions of the diffraction are as follows:

Current, voltage	20 mA, 30 KV
Time constant	10 seconds
Beam slit width	2 mm
Detector slit width	0.3 mm
Scanning speed	3^0/ min in 2θ
Full scale intensity	5,000 or 10,000 cpm

A computer recorded all intensity versus angle data via an interface and latter plotted using software. The position of peak, corresponding relative intensities and the interplanar spacing (d) were obtained from the computer. The d values were calculated by using Bragg's formula

$$n\lambda = 2d \sin\theta$$

where n = order of reflection (1), λ = wavelength of incident x-ray (1.54184 Å), d = interplanar spacing and θ = angle of diffraction.

The phase analysis and indexing of the peaks were done by ... the ... positions and relative intensities with standard data (JCPDS files).

2.5 BET SURFACE AREA MEASUREMENT

The surface area was measured by using a COULTER SA3100 instrument. Dry nitrogen and helium were used as an adsorbent and carrier gas respectively. First of all a definite amount of sample was weighed and this was degassed at 120^0C for 30 minutes and then weighed again to determine the losses. Minimum of 0.1 gram of powder is required for surface area measurement. The tube containing the sample was then evacuated and maintained at liquid nitrogen temperature by putting it in a flask filled with liquid nitrogen. Dry nitrogen gas was passed through the tube and the adsorption isotherm was observed. Then the liquid nitrogen flask was removed. The sample tube came to the room temperature and the desorption isotherm was observed. The surface area was then calculated from the adsorption and desorption isotherm using BET equation.

The particle size was also calculated, using the specific surface area data, by the equation:

$$\phi = \frac{6}{S \rho}$$

where ϕ is the average diameter of a spherical particle, S is the surface area of a powder, and ρ is the density value of sample.

CHAPTER 3

RESULTS AND DISCUSSION

As was discussed in earlier chapter, the instrument for particle size measurement in the nanometer range had been newly acquired and needed calibration. For this purpose various samples were used. These include latex standard sample (200 nm nominal size, Duke Scientific Co., supplied by Malvern Instruments, U.K), alumina (high purity alumina, Sumitomo Chemical Co. Ltd., Japan, AKP – 50, 0.2 μm nominal size), and ZrO_2 powder (supplied by TOSOH, Japan, nominal size 0.2 μm).

The details of preparation of the above mentioned samples under various conditions have already been described in section 2.1. The results of the calibration runs made using these samples are given below:

After describing the experiments carried out to calibrate the instrument, the preparation of zirconia powders by homogeneous precipitation is described.

3.1. CALIBRATION RUNS

3.1.1. Calibration runs with latex standard samples

The preparation of latex standard samples suspended in 10 mM of NaCl solution and in distilled water is described in section 2.1.1. Particle sizes of latex samples measured by HPPS under various conditions are given in Table 3.1.1.

Table 3.1.1. Particle size of latex standard sample measured by HPPS

Sl No	Nature of suspending media	Particle size (nm): HPPS				
		Run no.	Diameter	Average Diameter	PDI	Average PDI
1.	Water (not filtered) η = 0.899 cPs μ = 1.33 T= 25⁰C	1	198	209	0.042	0.052
		2	203		0.059	
		3	208		0.043	
		4	208		0.074	
		5	211		0.043	
		6	213		0.043	
		7	213		0.062	
		8	212		0.068	
		9	211		0.034	
2.	Water (filtered through 0.22 μm filter paper) η = 0.899 cPs μ = 1.33 T= 25⁰C	1	194	200	0.007	0.018
		2	201		0.033	
		3	200		0.013	
		4	195		0.028	
		5	203		0.007	
		6	201		0.028	
		7	202		0.005	
		8	201		0.026	
		9	202		0.014	
3.	10 mM NaCl solution (with filtered water) η = 0.899 cPs μ = 1.33 T= 25⁰C	1	213	216	0.067	0.057
		2	213		0.067	
		3	213		0.041	
		4	220		0.041	
		5	219		0.071	
		6	220		0.069	
		7	217		0.001	
		8	213		0.086	
		9	218		0.077	

3.1.2. Calibration runs with alumina

The preparation method of 0.001, 0.005, 0.1 and 1.0 volume percent

of alumina suspensions at various conditions are described in section 2.1.2. Particle

sizes measured by HPPS using different samples are given in Table 3.1.2.

Table 3.1.2. Particle size of alumina measured by HPPS using suspensions of different concentrations

Sl No	Vol % of Sumitomo alumina	Settling time	Largest Calculated Particle size (nm)	HPPS Programme			HPPS result		
				No. of runs	Run duration (s)	No. of measurement	Avg Dia (nm)	Avg Width (nm)	Avg PDI
1.	0.001	0	-	6	10	2	1490	476	0.406
2.	0.005	0	-	6	10	2	3543	1245	0.494
3. (a)		1 hr and 30 mins	~1000	10	10	3	2461	793	0.419
(b)	0.1	0	-	10	10	2	1016	343	0.457
(c)		16 hrs	408	31	10	3	444	128	0.331
(d)		0	-	31	10	3	291	73	0.252
4. (a)	1	8 hrs and 30 mins	212	-	160	-	185	45	0.232
(b)	1 (water was filtered through 0.22 μm filter paper)	0	200	-	170	-	194	52	0.291
(c)	1 (original solution was diluted to 100%)	0	200	21	10	3	211	48	0.207

In the case of experiments 1, 2, 3(a), 3(b) and 3(c) the measured particle size shows large deviations from the nominal size (200nm) or the size expected from the sedimentation time. However, in experiments 3(c), (d) and 4(a), (b) and (c), the measured and the actual particle size are quite close. The difference in the two sets of measurements is the following. In the first set of experiments the measurement was carried out in the 'custom' mode in which the number of runs per

measurement and the run time were kept equal to or below 10 and 10 sec respectively. In the later set, the instrument was allowed to set these parameters itself (normal mode). In this case the number of runs were much larger than 10 (21 or 31). Correct results were obtained in the normal mode irrespective of the concentration of the suspension and the time of settling.

The conclusions from this set of experiments is that the HPPS is able to measure the size of alumina particles correctly in the 1 vol% to << 0.1 vol% suspensions when the measurements are carried out in the "normal" mode. If a "custom" mode in which the number of runs per measurement or the time per run is much less than the "normal" mode values, then the results obtained are erroneous.

3.1.3. Calibration runs by using TOSOH-ZrO₂ powder

The procedure for preparation of 0.005, 0.01, 0.02 and 0.03 volume percent TOSOH-ZrO_2 suspensions are described in section 2.1.3. The measurements were carried out in the normal mode. In Table 3.1.3 particle size of TOSOH-ZrO_2 measured by HPPS versus calculated particle size from Stokes' law is compared. It is seen that the agreement between the two is quite good.

Table 3.1.3. Comparison of particle size of TOSOH-ZrO_2 measured by HPPS versus calculated particle size from Stokes' law.

Sample details		Measured Visco sity (cps)	Gravity Settling time	Particle size (nm)		
Cocentra Tion of TOSOH-ZrO_2 (vol%)	HPC concentration (µM)			Calculated	Avg dia by HPPS	Avg width by HPPS
0.005	3.125	1.45	4 hours and 30 mins	221	199	39
0.01	3.125	1.40	6 hours	235	216	42
0.02	3.125	Not measured	24 hours	All particles settled down		

3.1.4. Calibration experiments: Summary and Conclusions

In the calibration runs described above, three sets of known samples were used to calibrate the HPPS. When the standard latex spheres of 200nm are used, the measured particle size comes out to be 8 % larger (216 nm measured vs 200 nm actual) under manufacturers specified conditions i.e. using filtered NaCl solution as the medium. However, this appears to be the consequence of not taking into account the increase in viscosity of water due to the addition of NaCl. It may be also be because of the use of a "custom" mode with less number of runs per measurement in the initial experiment. When only filtered deionized water is used, the measured value is same as the actual value (200nm).

With the other two samples, Al_2O_3 and ZrO_2, the measured value is in agreement with the nominal values. In the case of Al_2O_3, using the normal mode, the measured particle size is between 185 to 211 nm as compared to the nominal size of 200nm. For ZrO_2, the measured particle size is between 199 to 216 nm versus the nominal size of 200 nm.

In conclusion, it can be said that the HPPS is able to measure the particle size of latex spheres and oxide particles quite well when certain precautions are taken. These are (i) use of the normal mode of measurement, (ii) accurate measurement of the viscosity of the suspending liquid, (iii) use of filtered suspension medium, (iv) use of well-dispersed suspensions.

3.2.   PRECIPITATION   OF   ZrO₂   POWDERS   BY   UNIFORM PRECIPITATION

In this section the results on the preparation and characterization of the ZrO_2 particles by uniform precipitation are described. Certain discrepancies were encountered between the particle sizes measured by HPPS and TEM. Experiments carried out to resolve the discrepancy are also described.

Powders of hydrous zirconia were prepared by precipitation from a solution of $ZrOCl_2 8H_2O$ in water and alcohol by microwave heating as described earlier in section 2.2.1. A surfactant, hydroxypropyl cellulose (HPC) was also used during preparation to prevent agglomeration of the particles. The as prepared particles are therefore expected to have a layer of water and HPC molecules on their surfaces. This would change the diffusion coefficient of the particles. Hence the HPPS would measure a different particle size than the actual particle size without the water and HPC layer. To quantify this difference, experiments were carried out in which the particle size of the as prepared particles suspended in the mother liquor and measured by HPPS was compared with their size as measured by TEM after drying or heating. To vary the particle size, the parameters (a) $ZrOCl_2.8H_2O$ concentration and (b) HPC concentration were varied. The experiments described below establish the dependence of these parameters on the particle size, as well as help to calibrate the particle size of the as prepared powders in suspension.

3.2.1. Effect of zirconyl chloride concentration

To study the effect salt concentration on particle size and morphology, powders were prepared using 0.005, 0.01, 0.02, 0.05, 0.08 and 0.1M of zirconyl chloride concentration (details of preparation method are described in section

2.2.1). The microwave power and heating time were kept constant at 80% and 20 seconds respectively. HPC concentration was fixed at 21.25 micromolar (1.7×10^{-3} gm/cc) in all cases. Average particle size and standard deviation of as-prepared hydrous zirconia measured by TEM and HPPS are given in Table 3.2.1. Standard deviation in each case is converted to equivalent width at half maximum as described in Appendix-3.

Table 3.2.1 Average particle size and standard deviation at different salt concentrations measured by TEM and HPPS

Sl No.	Molar Concentration (M)	Preparation Condition	Measured Viscosity (cps)	TEM analysis		HPPS analysis	
				Avg Size (nm)	Avg standard Deviation (nm)	Avg Dia (nm)	Avg width (nm)
1.	0.005	Mother liquor (as prepared)	4.2	40	25	99	19
2.	0.01	Mother liquor (as prepared)	4.3	49	13	116	18
3.	0.02	Mother liquor (as prepared)	4.3	68	13	131	20
4.	0.05	35 drops of mother liquor dispersed in 15 ml of propanol containing 12.5 μm of HPC	3.0	187	79	217	21
5.	0.08	20 drops of mother liquor dispersed in 15 ml of propanol containing 12.5 μm of HPC	3.1	188	51	302	46
6.	0.1	15 drops of mother liquor dispersed in 15 ml of propanol containing 12.5 μm of HPC	2.95	281	85	384	45

Fig 3.2.1 shows the dependence of the particle size of powders on the concentration of $ZrOCl_2.8H_2O$ in the starting solution. The particle size was

measured in the mother liquor by HPPS. It is seen that the particle size increases nearly linearly with the salt concentration.

The particle size of these powders was also measured by TEM using a drop of the mother liquor dried on the TEM grid. Fig 3.2.2 compares particle size in mother liquor by HPPS with size by TEM in the dried mother liquor drop. It is observed from the figure that every data point lies to the right of the 45^0 line, which means that particle size measured by HPPS is larger. The most likely reason, as mentioned earlier, is the presence of a layer of HPC and water molecules grafted/adsorbed on the particles which leads to a lower diffusion coefficient of the particles and results in a higher particle size compared to corresponding particle size by TEM. The issue, whether the HPC particles are grafted on the particles or merely adsorbed on the surfaces, is still not very clear. Moon. et. al.[13] have concluded that the HPC molecules keep moving to the surfaces as the particle growth progresses. However, this may not be the case and the HPC molecules may actually be getting grafted on the particle surface. The slope of the best straight line fit to the data in fig 3.2.2 is 0.821. This means that the particle size by TEM is 0.821 times the particle size measured in the mother liquor by HPPS.

Fig 3.2.3 (a), (b), (c) and (d) show TEM micrographs of samples prepared using 0.01, 0.05, 0.08 and 0.1M $ZrOCl_2.8H_2O$ concentration respectively (details of preparation of specimens for TEM observation are described in section 2.3.2). TEM images show nearly a spherical nature of the particles.

The experiments described in this section show that (i) the particle size of the hydrous ZrO_2 particles increases nearly linearly with the salt concentration used and (ii) the actual particle size is smaller by a factor of 0.821 from the particle size measured in the mother liquor by HPPS. Thus the concentration of salt can be

concentration of 0.005 M. Furthermore, HPPS is sensitive to the presence of adsorbed polymer layers. It is shown later, that when the polymer layer is removed, the particle size as measured by the two techniques is the same.

3.2.2 Particle size by HPPS and TEM of the as prepared and calcined powders: the adsorbed water and HPC layers

The aims of this set of experiments were to (i) see if there is shrinkage in the particle size upon heating and (ii) what is the effect of complete removal of the polymer layer on the sizes as measured by HPPS and TEM.

The detailed preparation methods for zirconia powder with subsequent washing/drying, calcination and hydrothermal treatment are described in section 2.2. The powders prepared using 0.05 M and 0.1 M $ZrOCl_2.8H2O$ have been used. The powders have been characterized in four conditions --- a) in mother liquor, b) washed and dried, c) calcined at 600^0 C, 1 hour and d) calcined at 600^0 C, 6 hours followed by hydrothermal treatment at 230^0 C, 6 hours. Table 3.2.2 shows mean particle size and standard deviation measured by HPPS of zirconia powders as prepared and subjected to various treatments. The particle size was also measured by TEM in same cases and is included in the Table 3.2.2.

Fig 3.2.4 compares the particle size of zirconia powders as prepared and subjected to various treatments for 0.05 and 0.1 M $ZrOCl_2.8H_2O$ concentrations respectively. It is observed that in both cases particle size as measured by HPPS decreases with drying and calcination. In the case of the powder prepared using 0.1 M suspension, there is a large decrease in particle size of the dried powder as compared

Table 3.2.2 Mean particle size and standard deviation of zirconia powders as prepared and subjected to various treatments measured by TEM and HPPS.

Sl No.	Nature of sample		Particle size (nm): TEM		Particle size (nm): HPPS	
	Molar Concentration	Type of treatment	Avg size	Standard deviation	Avg Dia	Avg width
1.	0.1	Mother liquor	-	-	518	160
		Washed and dried	148	48	200	29
		Calcined at 600^0 C, 6 hrs followed by hydrothermal at 230^0 C, 6 hrs	160	42	163	22
2.	0.05	Mother liquor	-	-	313	26
		Washed, dried	196	70	283	34
		Calcined at 600^0 C, 1 hrs	205	71	287	58

to the size measured in the mother liquor. This is because during the washing of this sample, the first few washings were done using de-ionized water. This caused peptization of the particles. For the 0.05 M sample, washing water of pH 7.0-7.5 was used to prevent peptization of the particles. It is also observed that particle size as measured by TEM does not change much upon calcination [fig. 3.2.5 (a), (b), (c) and (d)].

It is observed that there is a good agreement between HPPS and TEM in the case of powder subjected to calcination at 600^0C, 6 hours followed by hydrothermal at 230^0C, 6 hours (Fig. 3.2.6). However, the particle size of the washed and dried powder and also of the powder further calcined at 600^0C for 1 hour is larger when measured by HPPS as compared with corresponding particle size by TEM. The reason for this discrepancy is attributed to the fact that the adsorbed HPC and water layer do not seem to be completely removed in the as dried powder as well as in the powder calcined at 600^0C, 1 hour; only the calcination at 600^0C/6 hours is able to

remove the layers completely. This is supported by the observation that the color of the powder becomes brownish after calcination at 600^0C, 1 hour. On the other hand, the color of the particles calcined at 600^0C, 6 hours is white as expected and particle sizes as measured by HPPS and TEM agree.

It should also be noted that the particle size as measured by TEM is same for the dried as well as the calcined powders. Hence to know the actual particle size by TEM, it is not necessary to calcine the powder – as dried powder can be measured by TEM to give the correct particle size.

3.2.3. Effect of the surfactant (hydroxypropyl cellulose, HPC) concentration on particle size

Effect of hydroxypropyl cellulose (HPC) on particle size and morphology was extensively studied. For this, $ZrOCl_2.8H_2O$ concentrations of 0.01 and 0.02 M were used. HPC concentrations were 1.875, 6.25, 9.375, 12.5, 18.75, 21.25 and 62.5 micromolar for 0.01M and 1.875, 6.25, 9.375, 12.5, 15.62 and 62.5 micromolar for 0.02M respectively.

Table 3.2.3 and Fig 3.2.7and 3.2.8 give the variation of particle size (measured by HPPS in mother liquor and by TEM) with HPC concentration for 0.01M and 0.02M salt concentration respectively. The particle size decreases from 254 nm to 109 nm for 0.01 M (Table 3.2.3) and from 512 nm to 202 nm for 0.02 M $ZrOCl_2.8H_2O$ respectively. It is observed that there is a very large decrease in particle size and the width of the distribution when the HPC concentration is increased from 1.875 to 6.25 μM. Increasing the HPC concentration beyond 6.25 μM causes only a slight decrease in the particle size and width. At the two highest HPC concentrations used for 0.01M $ZrOCl_2.8H_2O$ sample, the particle size as measured by HPPS is

reduced to ~110 nm average value with a width of 20 nm. The actual particle sizes (by TEM) are expected to be much smaller (~60 nm) under these conditions with a narrow ($\pm$10 nm) width. Nearly similar trends are obtained when the salt concentration is 0.02M. For this case the TEM micrographs (Fig 3.2.9 a, b and c) show that the particle size decreases from 133 nm to 68 nm when the HPC concentration increases from 1.875 to 21.25 μM. However in this case there is an increase in the HPPS particle size at the highest (62.5 μm) HPC concentrations, although the TEM size is much reduced (68 nm).

The effect of HPC can be explained by the steric stabilization from the adsorption of macromolecules onto the particle surface. Lower concentration of HPC is not sufficient for monolayer adsorption on particle surface and this could explain agglomerated particles and higher width at lower HPC concentration.

Table 3.2.3. Variation in particle size with HPC concentration for powders prepared using at 0.01 M and 0.02 M ZrOCl$_2$, 8H$_2$O concentration

Sl No.	Concentration of HPC (micromolar)	Particle size (nm): HPPS (TEM)			
		0.01M ZrOCl$_2$		0.02M ZrOCl$_2$	
		Average Dia	Average width	Average Dia	Average width
1.	1.875	254	39	512 (133)	142 (79)
2.	6.250	172	25	164 (87)	20 (35)
3.	9.375	155	24	165 (80)	19 (20)
4.	12.50	134	21	153 (83)	14 (19)
5.	15.02	--	--	122 (76)	18 (22)
6.	18.75	153	37	--	--
7.	21.25	113	22	-- (68)	-- (12)
8.	62.50	109	23	202	13

		8.50		3.90	115	13
3.	0.02	7.70	Mother liquor (as prepared)		130	20
		8.10		4.30	147	24
		2.0			130	16
4.	0.05	7.0	Mother liquor (as prepared)	5.10	243	40
		7.0		4.75	222	23
		8.20	35 drops of mother liquor dispersed in 15 ml of propanol containing 12.5 μm of HPC	2.80	217	21
		7.50	Mother liquor (as prepared)	4.60	203	12
		7.10	35 drops of mother liquor dispersed in 12 ml of propanol containing 12.5 μm of HPC	2.80	315	20
		7.30	35 drops of mother liquor dispersed in 15 ml of propanol containing 12.5 μm of HPC	3.00	313	27
5.	0.08	8.00	35 drops of mother liquor dispersed in 12 ml of propanol containing 12.5 μm of HPC	3.20	396	32
		7.00	20 drops of mother liquor dispersed in 15 ml of propanol containing 12.5 μm of HPC	3.10	302	47
6.	0.1	8.32	Measured after 2 months (ultrasonicate before measurement)	3.95	445	78

		6.70	15 drops of mother liquor dispersed in 15 ml of propanol containing 12.5 μm of HPC	2.70	384	45
		7.50	20 drops of mother liquor dispersed in 12 ml of propanol containing 12.5 μm of HPC	2.95	351	29

Fig 3.3.1 gives result of several measurements to test the reproducibility of the preparation method. It is observed that samples of 0.005, 0.01 and 0.02 M are nicely reproducible. But for higher molar concentration of $ZrOCl_2$. $8H_2O$ viz. 0.05, 0.08 and 0.1, reproducibility is somewhat less. This may be inherent for higher concentration precursors or it may be an artifact arising out due to further preparation of mother liquor in the case of high concentration precursors for better dispersion before measurement by HPPS. Figure 3.3.1 can be interpreted to indicate that the process is reproducible but the width of the particle size distribution increases with increased concentration of salt in the precursor solution.

3.4. DISSOLUTION KINETICS OF HYDROUS ZIRCONIA SUSPENDED IN MOTHER LIQUOR

Dissolution kinetics of hydrous zirconia in mother liquor was also studied by taking 0.02 M $ZrOCl_2.8H_2O$ concentration. The sample preparation is described in section 2.2.6. Microwave power input, heating time were kept at 80% and 20 second respectively and HPC concentration was 21.25 micromolar. pH of hydrous zirconia was kept as ~1.90. Variation of particle size with various time interval measured by HPPS is given in Table 3.4.1.

Table 3.4.1. Variation of particle size of hydrous zirconia with various time interval measured by HPPS

Sl No.	Time interval (min)	Particle size (nm): HPPS	
		Average diameter	Average width
1.	20	130	32
2.	50	131	40
3.	170	130	40
4.	210	131	29
5.	315	131	35
6.	420	132	44
7.	1140	132	39
8.	1170	135	45
9.	1380	130	38
10.	1440	134	38
11.	1620	130	38
12.	2460	153	72
13.	3195	132	27
14.	3210	133	34
15.	3930	130	23
16.	3960	128	47

Jindal[16] reported that the size of the particles of hydrous zirconia decreased initially, then increased and again decreased with time if the solution was allowed to stand. But in the present study, it is found that particle size is almost constant over a period of 66 hours (Fig 3.4.1). This can be explained as since HPC effectively inhibits particle agglomeration therefore interaction among the particles is less due to presence of HPC. So particle size does not change with time.

Earlier in section 3.2.2, it was found that the size of the particles decreases during washing with deionized water. In that case the pH was ~ 4.0. Hence

it appears that the dissolution (peptization) of the particles occurs only in a certain pH range (about the pH 4).

3.5. CHANGES IN STRUCTURE, PARTICLE SIZE AND SURFACE AREA ON HEATING

Amorphous powder of hydrous zirconia of 0.05 and 0.1 M $ZrOCl_2$. $8H_2O$ concentrations were synthesized by keeping microwave power 80% and heating time 20 seconds as discussed in section 2.2.1. The powders were then washed and dried as described in section 2.2.2. These dried powder were then subjected to calcination at 200^0, 400^0 and 600^0 C respectively. X-ray diffractograms [Fig 3.5.1 and 3.5.2] of both sets of powders show that powders were amorphous after the 200^0 and 400^0C treatments, but crystalline after the treatment at 600^0C. The phases present are monoclinic and cubic in both cases.

Particle size of 0.05 and 0.1 M $ZrOCl_2,8H_2O$ concentration samples at various conditions measured by TEM and HPPS is given in Table 3.5.1. TEM micrographs of some of the samples are given in Fig 3.2.5. (a), (b), (c) and (d).

It can be seen from Table 3.5.1 that the particle size does not change upon heating upto 600 ^0C. Then BET surface area was measured (Table 3.5.2) by using a COULTER SA3100 instrument. Average particle size was also calculated (Table 3.5.2) from measured surface area by using the formula given in section 2.5. The surface area of the powders showed a drastic change. Table 3.5.2 gives the surface area and the corresponding particle size calculated assuming the particles to be monosized spheres of theoretical density. The surface area decreases from about 90 m^2/gm to ~16 m^2/gm upon calcination at 600 ^0C. This shows that the as prepared dried powders have significant internal porosity. As the particle size does not change,

Table 3.5.1. Particle size of 0.05 and 0.1 M ZrOCl$_2$. 8H$_2$O at various conditions measured by TEM and HPPS

ZrOCl$_2$. 8H$_2$O concentration (M)	Treatment done	Particle size (nm): TEM		Particle size (nm): HPPS	
		Avg size	Avg standard deviation	Avg dia	Avg width
0.05	Mother liquor (as prepared)	-	-	314	53
	Washed, dried (as prepared)	196	70	283	35
	Calcined at 200^0 C, 1 hour	-	-	352	100
	Calcined at 400^0 C, 1 hour	-	-	324	85
	Calcined at 600^0 C, 1 hour	205	71	287	58
0.1	Mother liquor (as prepared)	-	-	518	160
	Washed, dried (as prepared)	148	48	200	29
	Calcined at 200^0 C, 1 hour	-	-	381	104
	Calcined at 400^0 C, 1 hour	-	-	328	87
	Calcined at 600^0 C, 1 hour	-	-	282	60
	Calcined at 600^0 C, 6 hour and followed by hydrothermal at 230^0 C, 6 hours	160	42	163	22

Table 3.5.2. BET surface area and average particle size for 0.05 M ZrOCl$_2$. 8H$_2$O concentration subjected to various treatments.

Sl No.	Treatment done	BET surface area (m^2/gm)	Average particle size (nm)
1.	Washed, dried	90	11
2.	Calcined at 200^0 C, 1 hour	Not measured	Not measured
3.	Calcined at 400^0 C, 1 hour	27	37
4.	Calcined at 600^0 C, 1 hour	16	64

only the surface pores are getting sealed off due to heating with the internal porosity remaining intact.

3.6 DISCUSSION

One of the difficulties in the characterization of nano particles is the uncertainty in the particle size measurement. In most of the literature on nanoparticle preparation and characterization, either TEM or x-ray line broadening results are presented. The disadvantages of these methods is that the TEM technique is tedious and provides limited statistics while the x-ray line broadening gives only an average crystallite size rather than the particle size. The use of dynamic light scattering apparatus removes these difficulties but requires caution in use and interpretation. It was for this reason that these measurements were carried out. On the whole it seems that the instrument can be used with confidence and can be exploited to also detect the presence of adsorbed layer if any.

In an earlier work in our laboratory (Jindal [16]), the powders were prepared without the use of a suitable surfactant. In this case the particles had a smooth, spherical morphology but they were mostly fused together. The use of HPC leads to well dispersed particles but their surfaces appears to be less smooth. Also the particle size distribution is much wider.

It appears possible to adjust the particle size of the as prepared particles by controlled peptization at suitable pH. This aspect needs further work.

The tentative conclusion about the particles being porous and only the surface pores getting sealed on calcinations at 600^0C also needs confirmation.
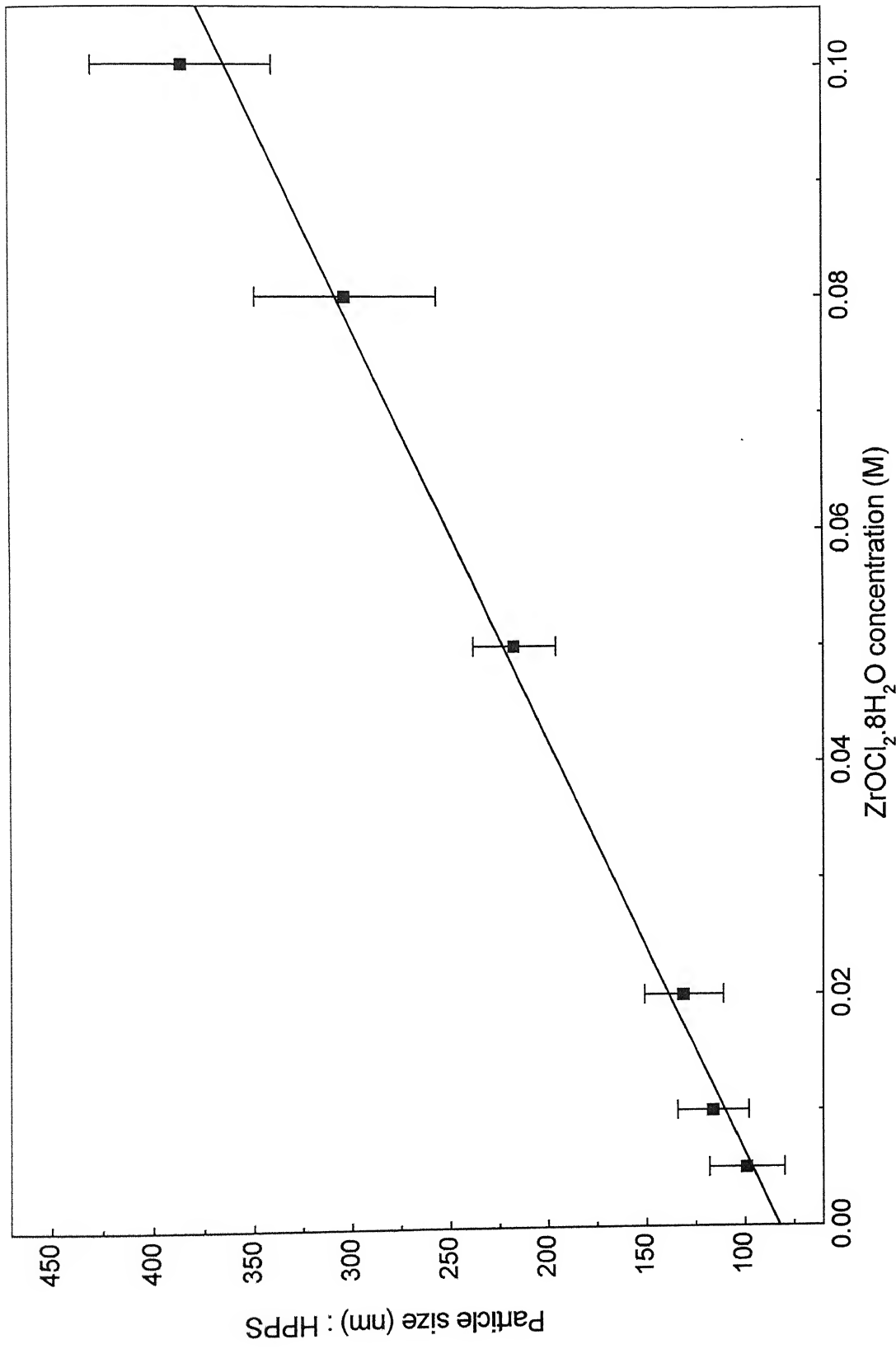
Fig 3.2.1 : Variation of particle size (measured in mother liquor) with $ZrOCl_2.8H_2O$ concentartion (M) at a fixed HPC concentration (21.25 micromolar)
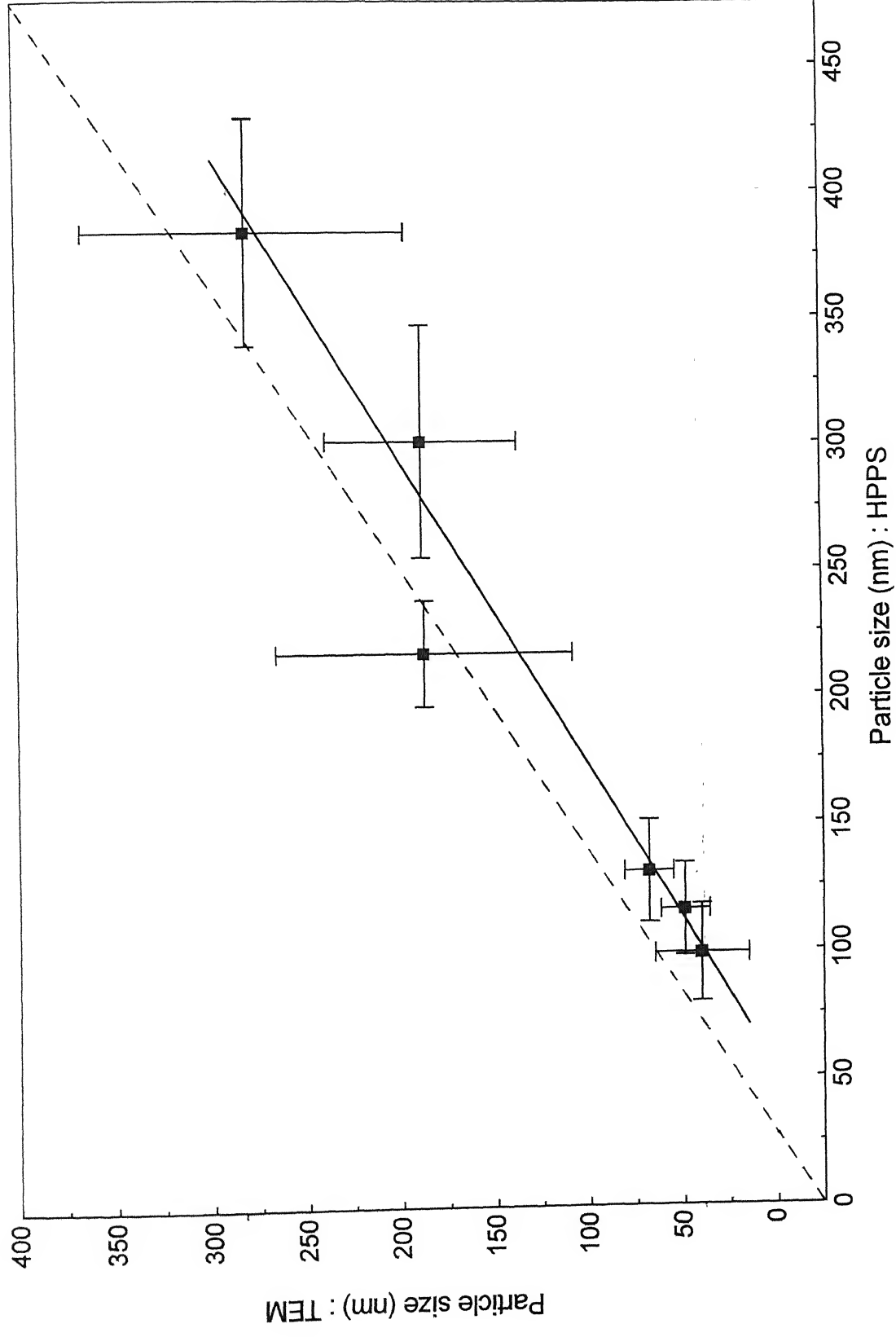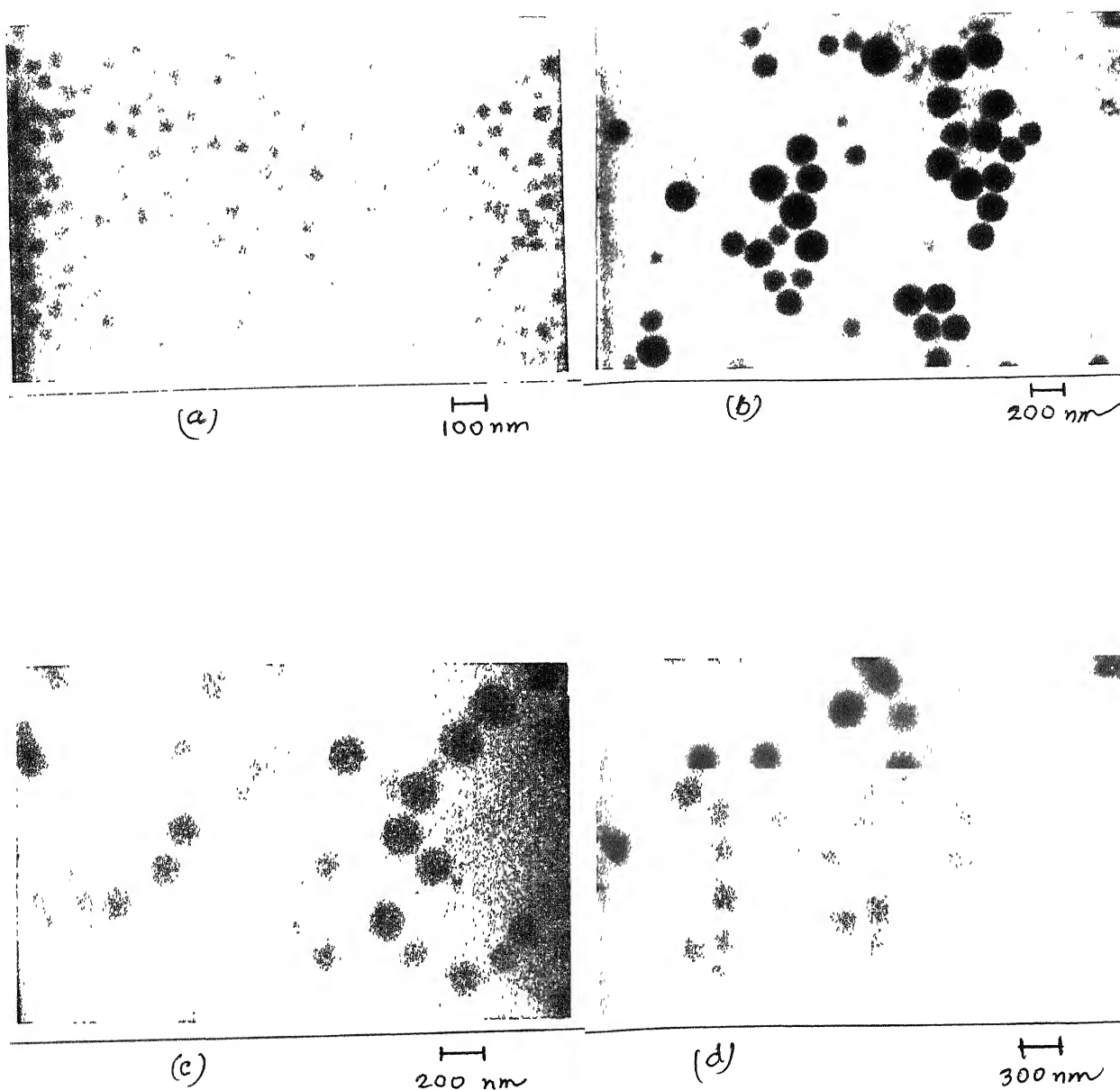
Fig 3.2.2 : Particle size in mother liquor by HPPS vs size by TEM in the dried mother liquor drop for samples prepared using different concentration of $ZrOCl_2.8H_2O$

Fig 3.2.3 TEM micrographs of hydrous zirconia (measured in dried mother liquor drop) synthesized by keeping microwave power 80%, time 20s, HPC 21.25 μM and salt concentration of 0.01M (a), 0.05M (b), 0.08M (c) and 0.1M (d)
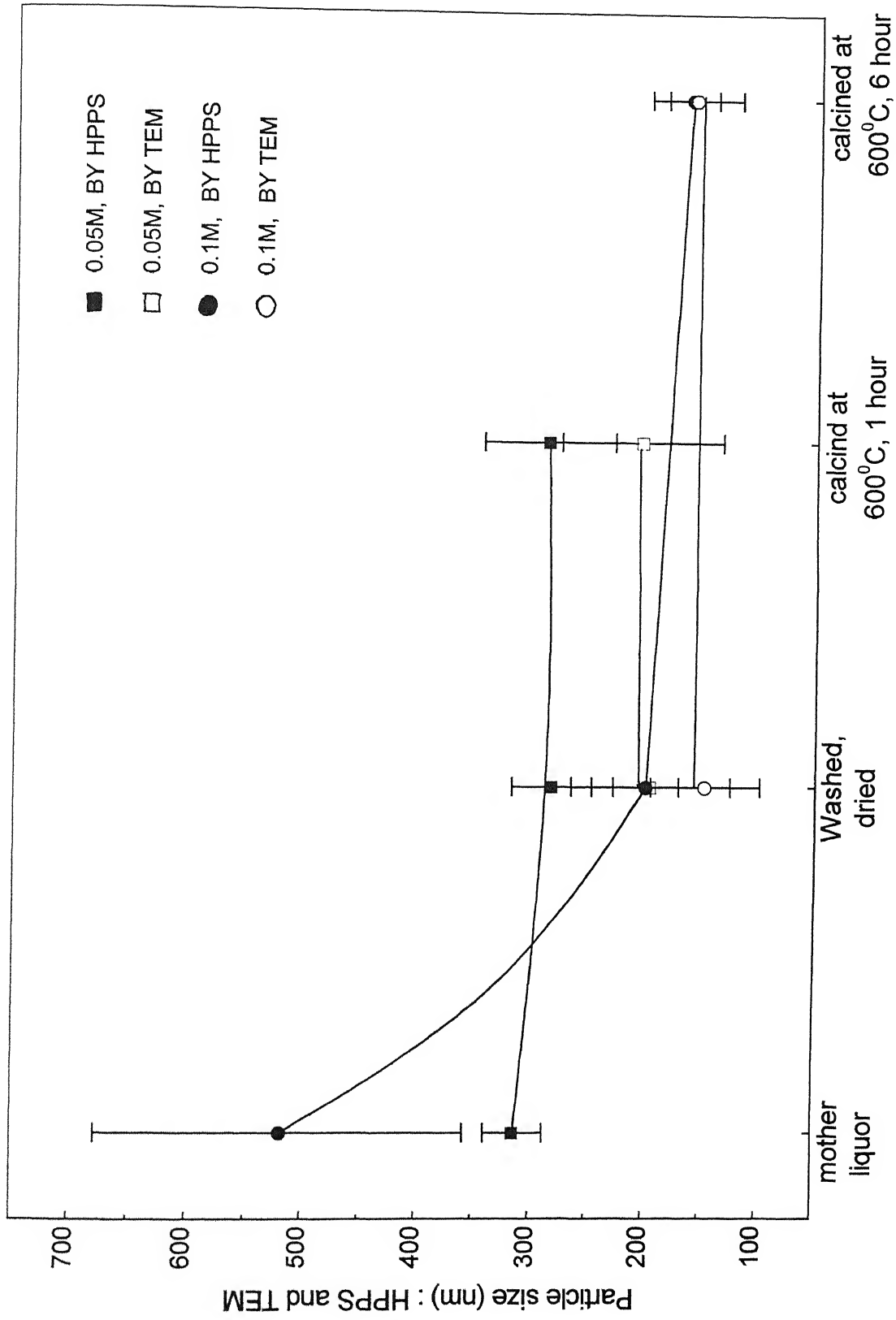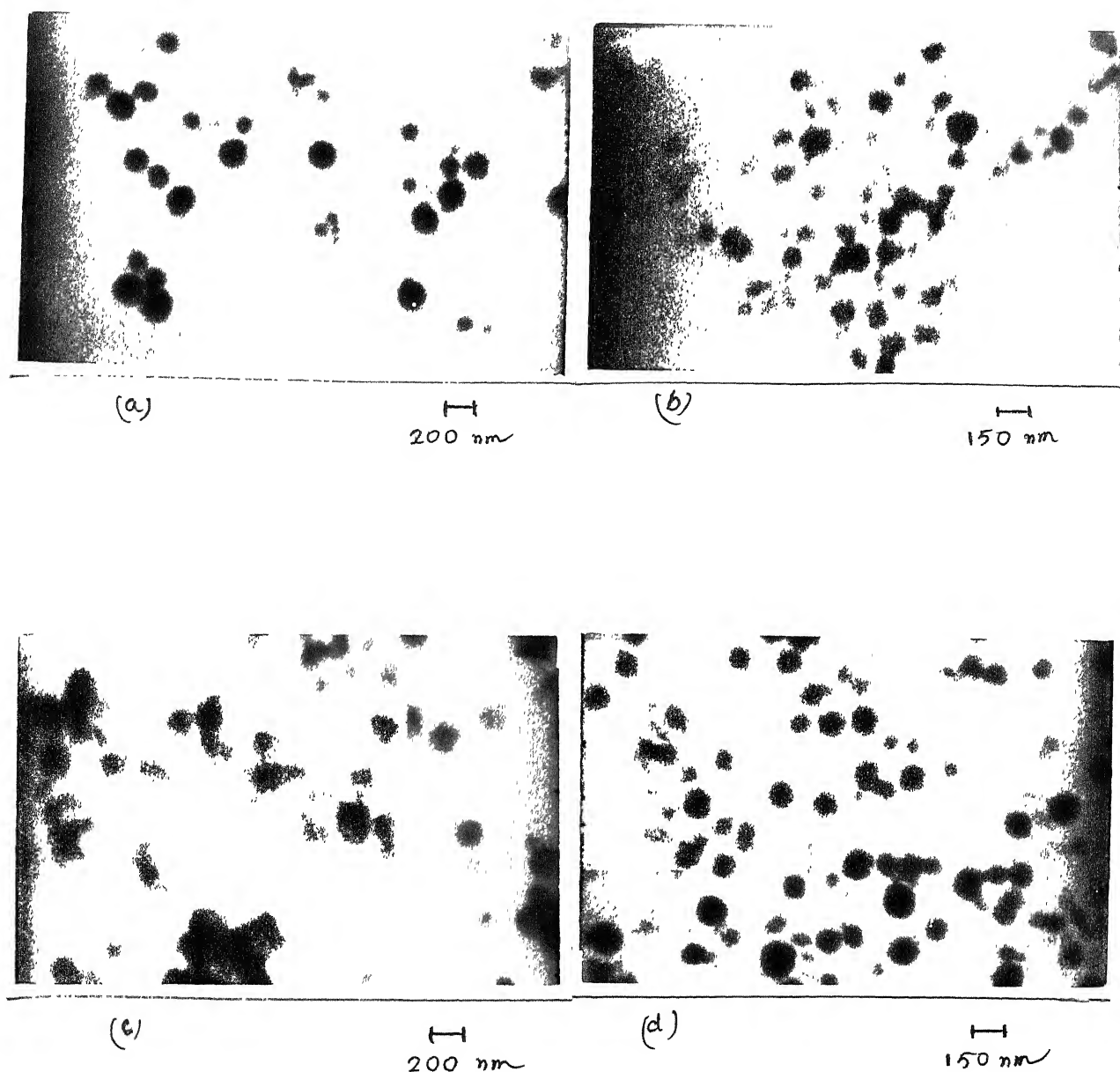
Fig 3.2.4 : Particle size of 0.05 and 0.1 M $ZrOCl_2,8H_2O$ concentration subjected to various treatment measured by TEM and HPPS

(a)

⊢—⊣
200 nm

(b)

⊢—⊣
150 nm

(c)

⊢—⊣
200 nm

(d)

⊢—⊣
150 nm

Fig 3.2.5 TEM micrographs of powders prepared at following conditions: (a) washed, dried, salt concentration 0.05M, (b) calcined at 600^0C, 6 h and then hydrothermal treatment at 230^0C, 6 h, salt concentration 0.1M, (c) calcined at 600^0C, 1 h, salt concentration 0.05M and (d) washed, dried zirconia powders, salt concentration 0.1M.
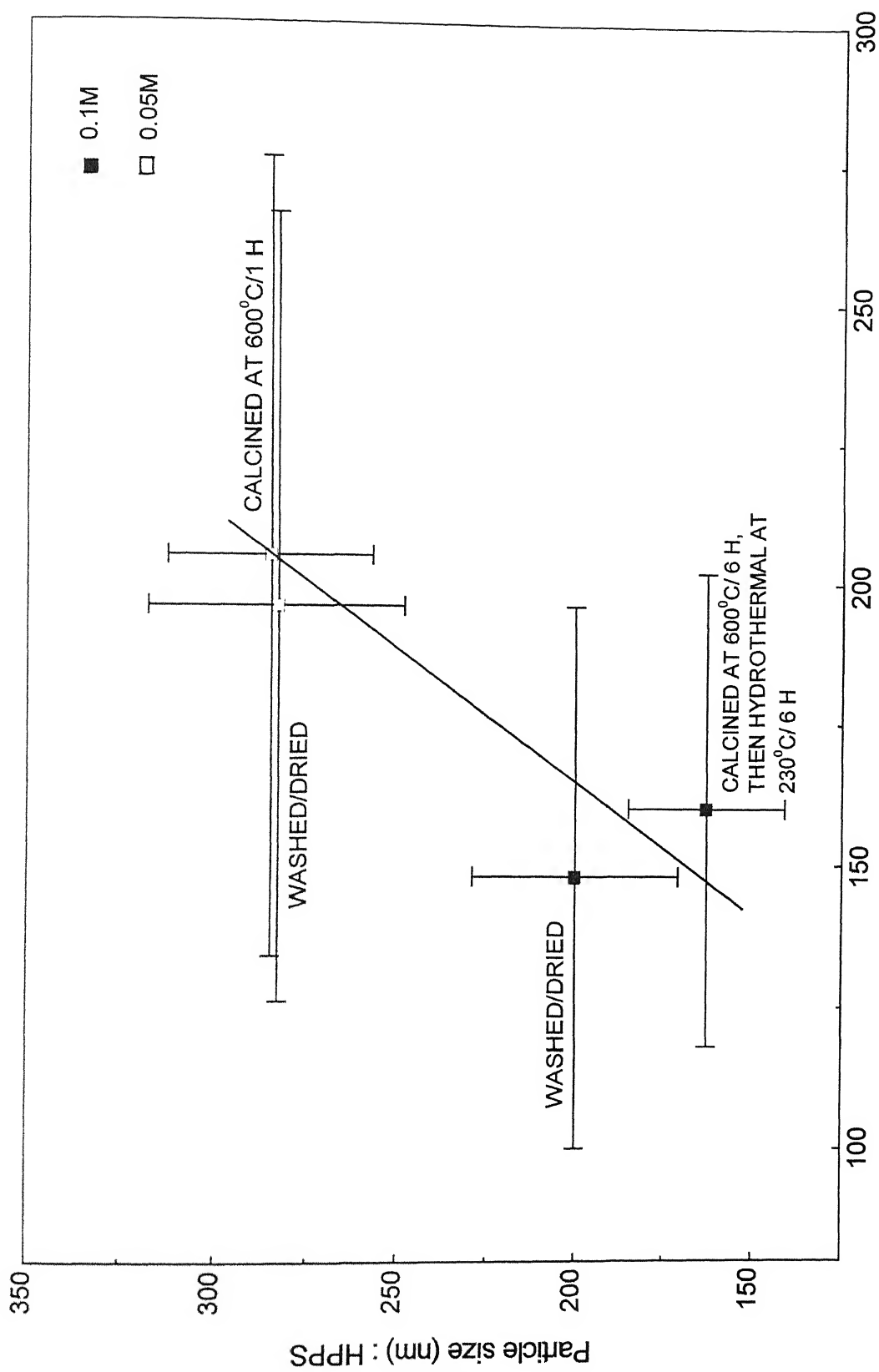
Fig 3.2.6: Particle size of dried ZrO_2 (as prepared and subjected to various treatment) by HPPS vs size by TEM
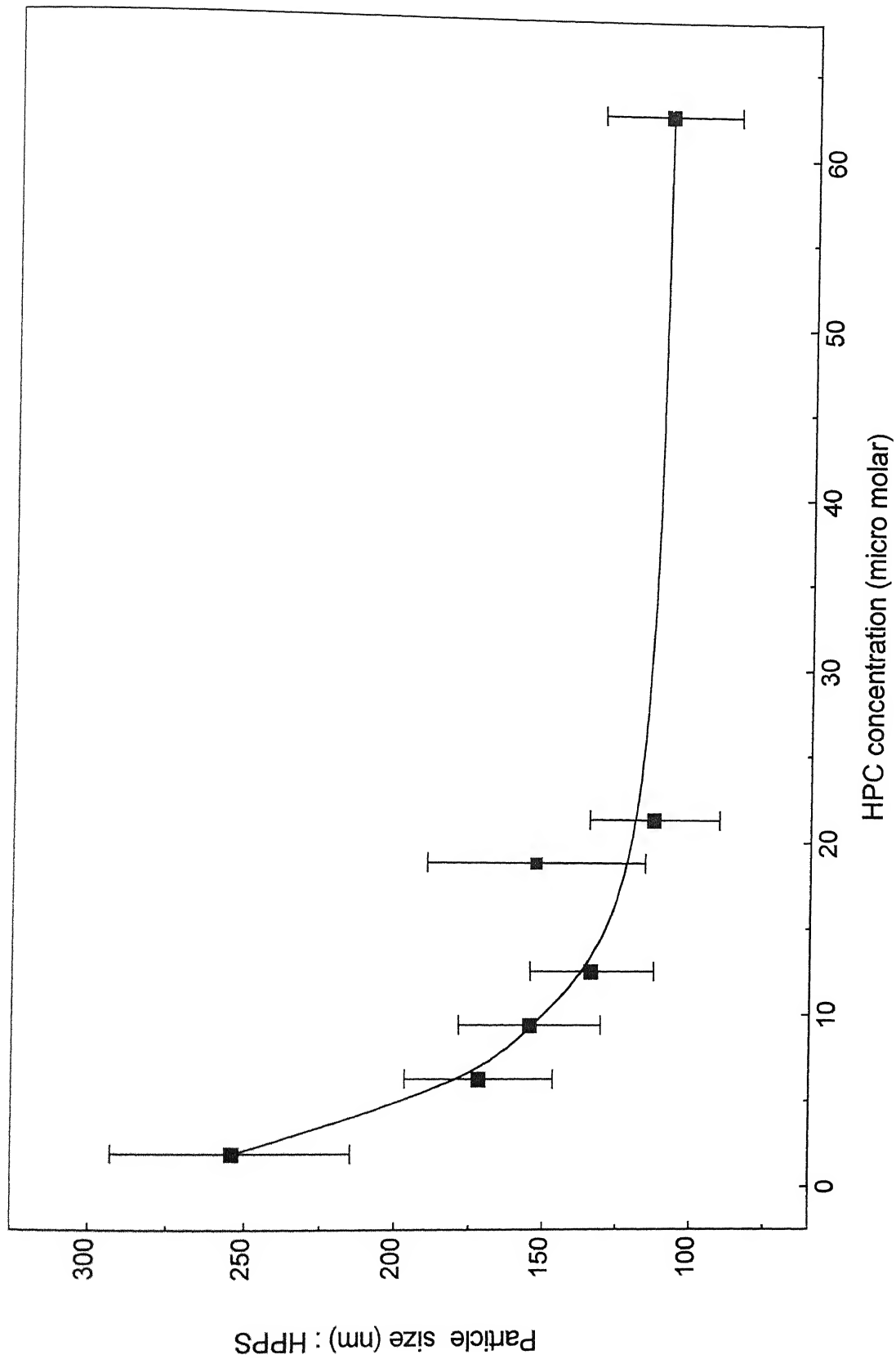
Fig 3.2.7 : Variation of particle size (measures in mother liquor) with HPC concentration at a fixed ZrOCl$_2$ concentration (0.01M)
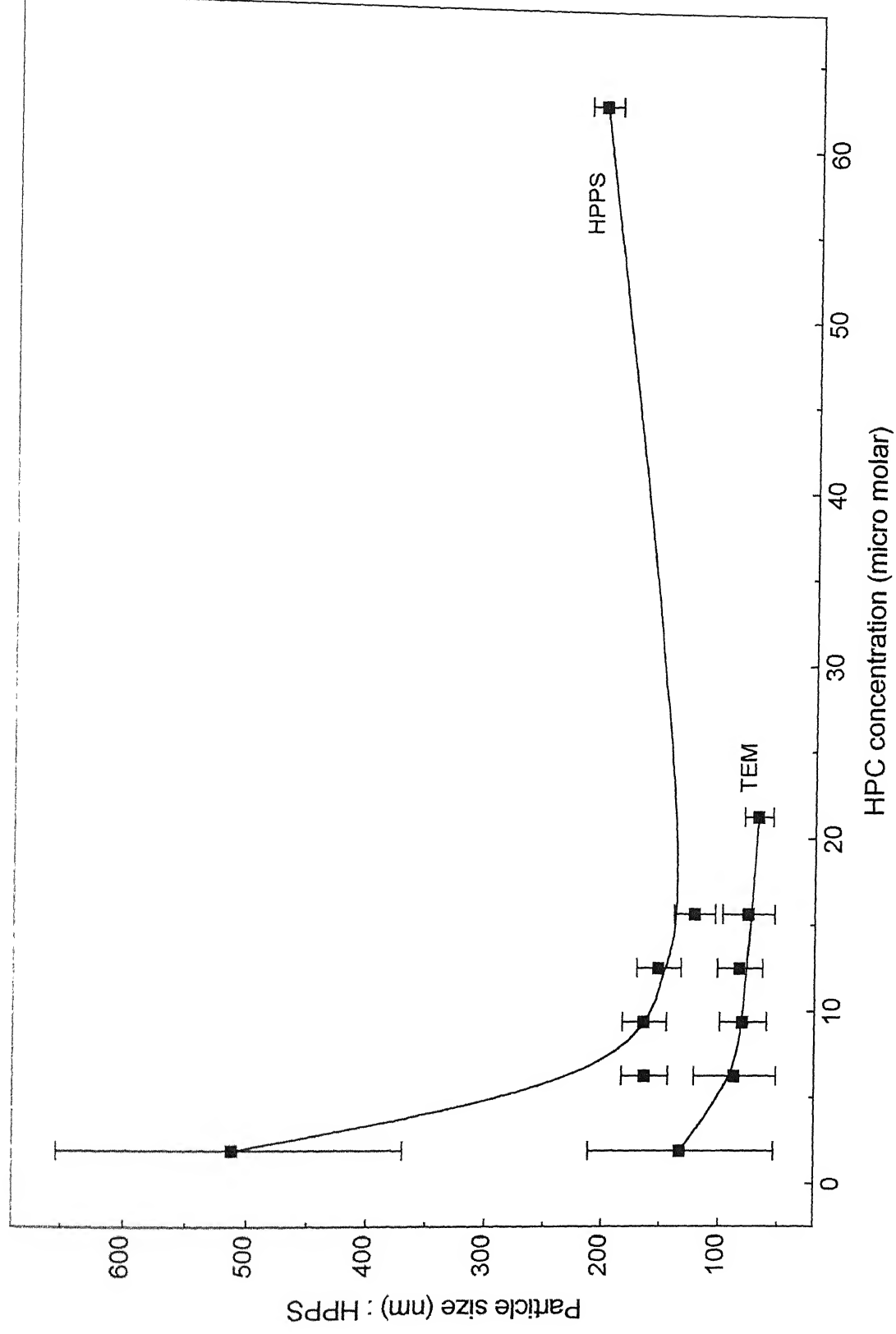
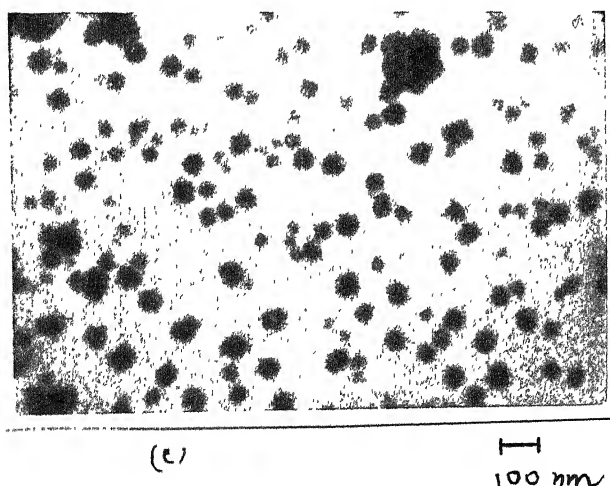Fig 3.2.8 : Variation of particle size (measured in mother liquor) with HPC concentration at a fixed $ZrOCl_2$ concentration (0.02M)

(a)

⊢—⊣
150 nm

(b)

⊢—⊣
100 nm

(c)

⊢—⊣
100 nm
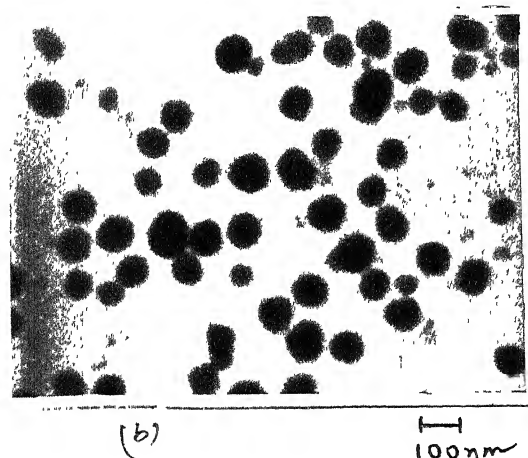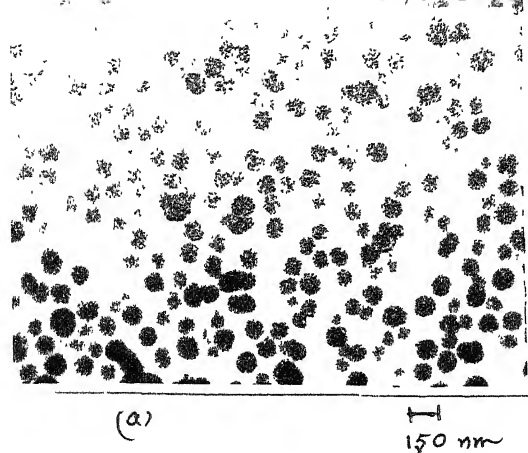
Fig 3.2.9 TEM micrographs (measured in dried mother liquor drop) showing particles of hydrous zirconia synthesized by keeping microwave power, time of heating and salt concentration at 80%, 20s and 0.02M respectively. HPC concentration was varied as 9.375 μM (a), 12.5 μM (b) and 21.25 μM (c).
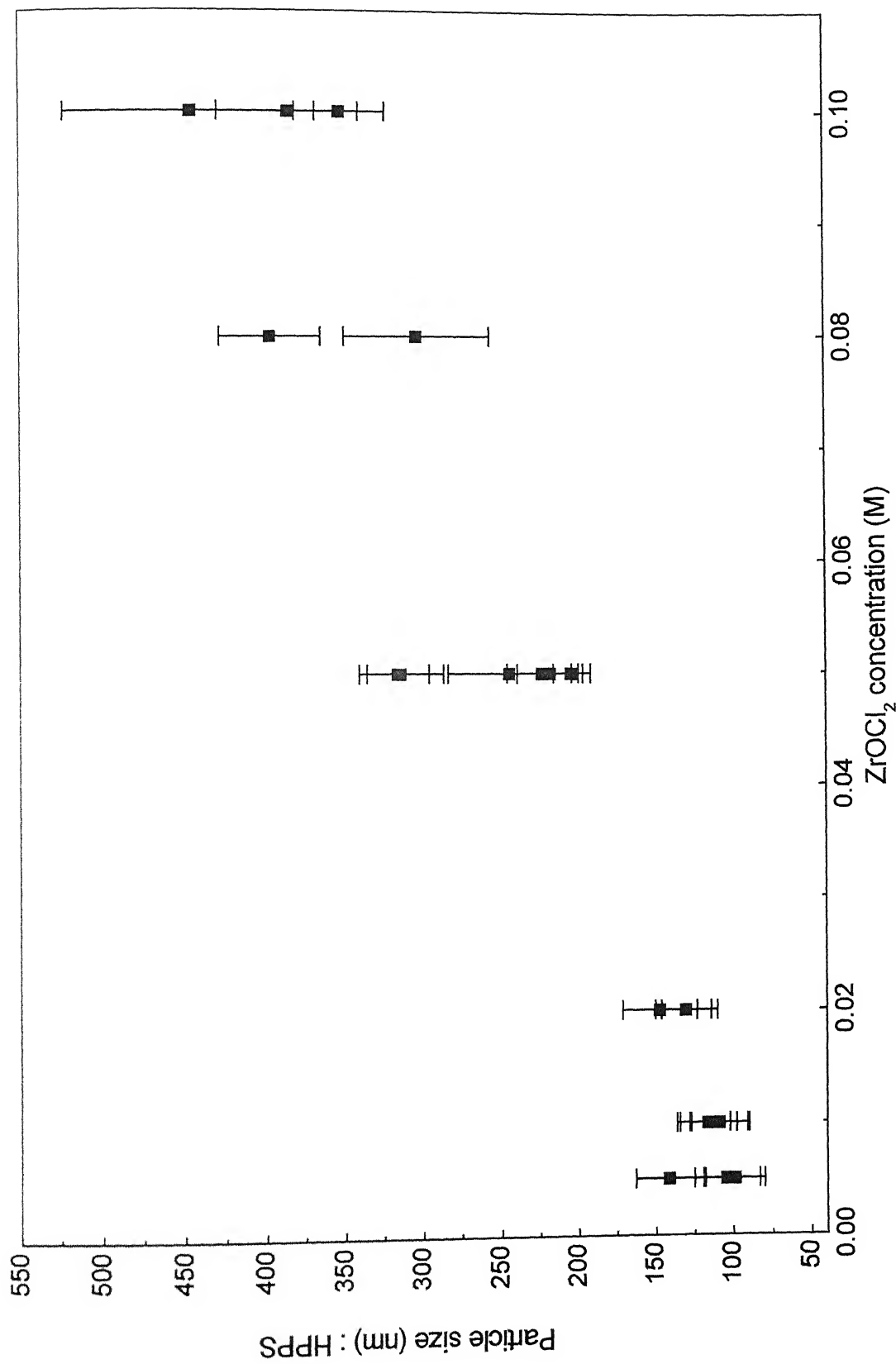
Fig 3.3.1: Results of several measurements to test reproducibility of the preparation method ----- each square shows the average result for one sample
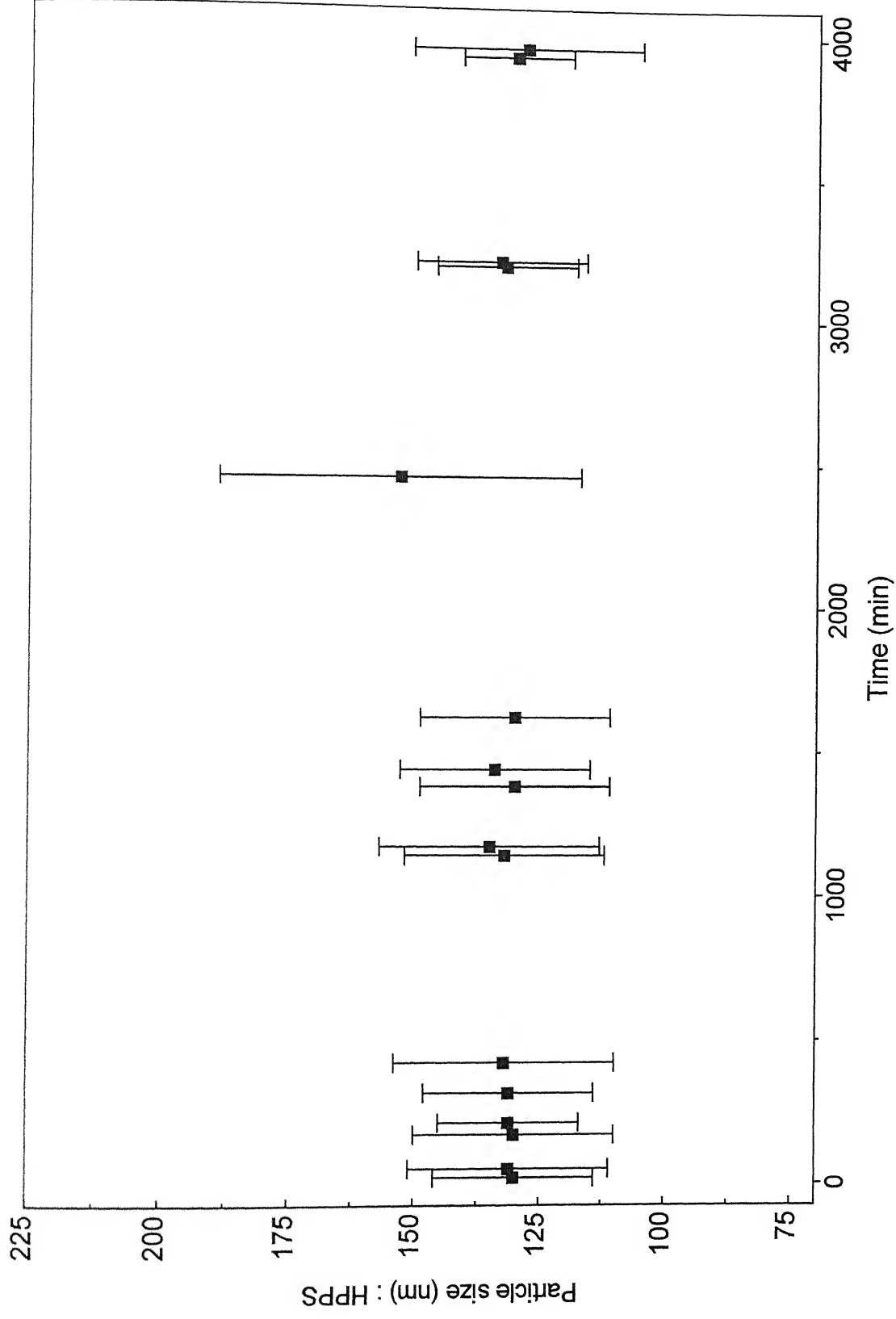
Fig 3.4.1 : Particle size of hydrous zirconia in mother liquor measured by HPPS at various time interval
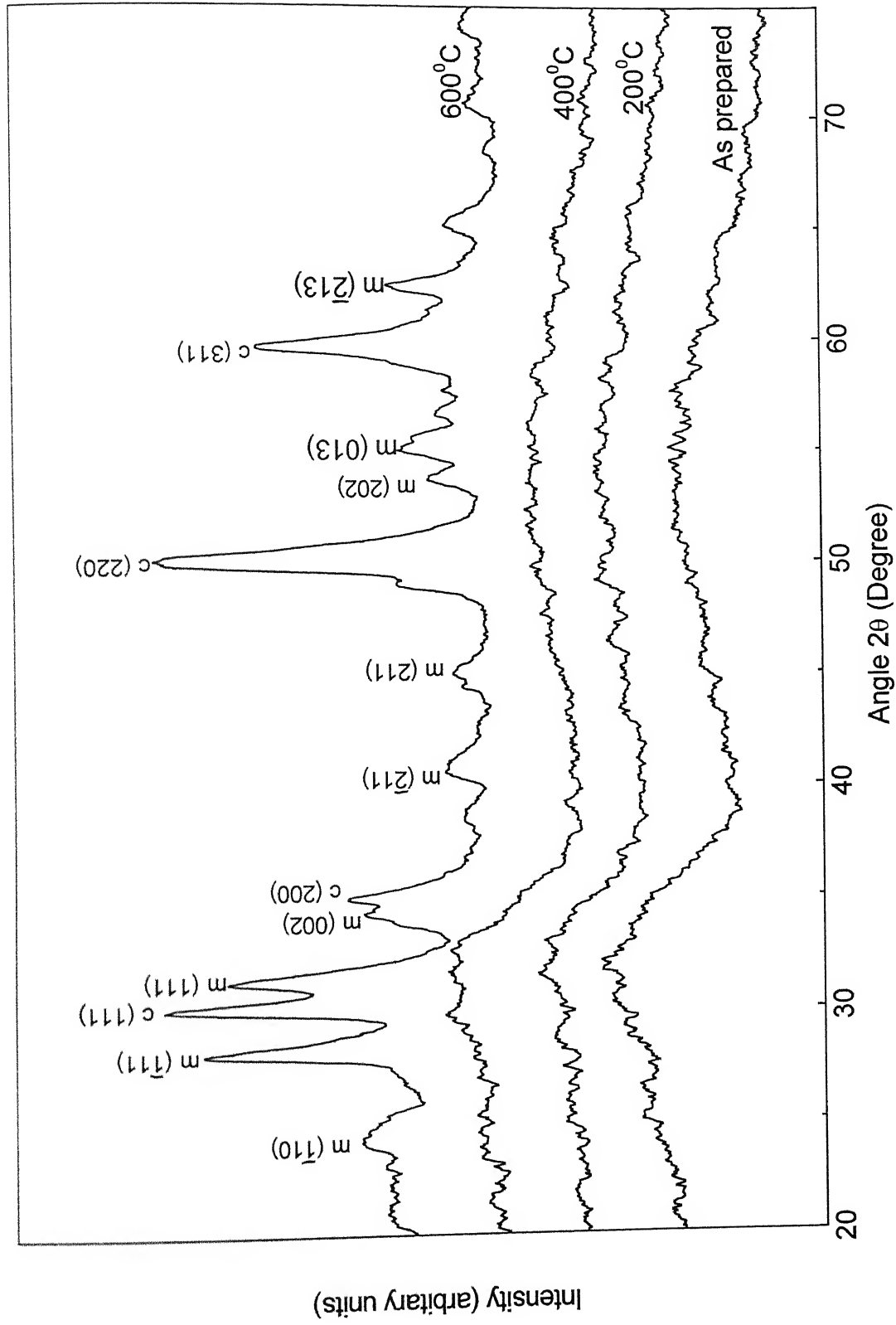
Fig 3.5.1: X-ray diffractograms of powders from 0.05M concentration $ZrOCl_2,8H_2O$ after calcination at different temperatures for one hour

Fig 3.5.2: X-ray diffractograms of powders from 0.1 molar concentration $ZrOCl_2,8H_2O$ after calcination at different temperature for one hour

SUMMARY AND CONCLUSIONS

The major aim of the present study was two fold (i) to properly calibrate the newly procured High Performance Particle Sizer (HPPS) and (ii) to prepare and study the dependence of particle size and morphology of hydrous zirconia particles on different processing parameters.

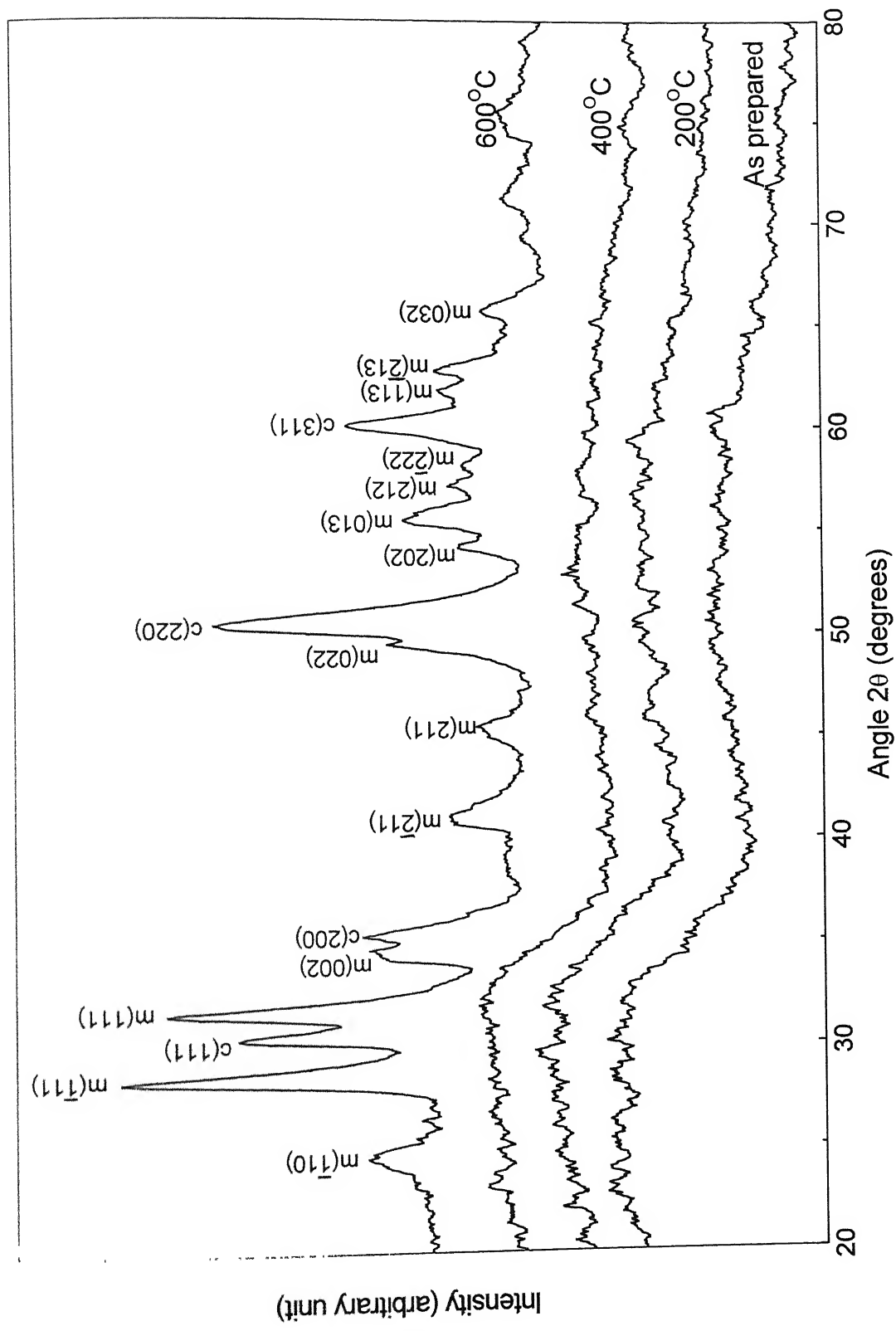For calibrating the HPPS instrument three sets of samples, i.e. standard latex spheres, Sumitomo alumina and TOSOH-zirconia powders of known sizes were used. In case of the standard latex spheres, the particle size came out to be 8% larger (216 nm measured versus 200 nm actual) when filtered NaCl solution, as specified by the supplier, was used as the suspending medium. This small discrepancy is attributed to the fact that the instrument was run in the 'custom' mode rather than the 'normal' mode and also because the viscosity value that for water was used rather than the NaCl solution. In case of the Al_2O_3 and ZrO_2 particles, the measured particle size was in between 185 nm to 211 nm (nominal size 200 nm) and 199 nm to 216 nm (nominal size 200 nm) respectively when the instrument run in the 'normal' mode. Thus there was a good agreement between the measured and nominal particle size.

These results showed that reliable results are produced by HPPS if certain precautions are taken. These are (i) the instrument should be run in the 'normal' mode, (ii) correct value of the viscosity of the suspending medium should be used, (iii) filtered suspension medium should be used, and (iv) the suspension should be well dispersed.

A homogeneous precipitation technique of heating alcohol-water solution containing zirconyl chloride salt and hydroxypropyl cellulose (used as a surfactant) was used for the preparation of zirconia particles. It was found that the

molar concentration of $ZrOCl_2$ has a direct effect on the particle size of hydrous zirconia; the particle size can be controlled by suitably selecting the initial concentration of $ZrOCl_2.8H_2O$. The particle size of hydrous zirconia measured in mother liquor by HPPS was found to be larger than that measured by TEM after drying a drop of the mother liquor on the TEM grid. Thus the particle size for 0.005, 0.01, 0.02, 0.05, 0.08 and 0.1M concentrations were 40, 49, 68, 187, 188, 281 nm by TEM and 99, 116, 131, 217, 302 and 384 nm by HPPS respectively. It is believed that a layer of HPC/water molecules grafted/adsorbed on the particle surface reduces the diffusion co-efficient of the particles resulting in higher numbers for particle size by HPPS.

It was found that the particle size by TEM and HPPS showed a good agreement in case of dried powders calcined at 600^0C, 6 h followed by hydrothermal treatment at 230^0C, 6 h. It implies that prolonged heating at higher temperature causes complete removal of HPC layer from the surface. The color of he powders also supports this conclusion, i.e. after heating at 600^0C, 1 h powders became brownish while calcination at 600^0C, 6 h yielded powders white in color.

HPC is found to be very effective in producing nanosized and well dispersed particles of hydrous zirconia. It was found that when the HPC concentration was increased from 1.875 to 6.25 micromoles, there was a large decrease in particle size and the distribution width. Increase of HPC beyond this value resulted in only a slight decrease of the particle size.

Hydrous zirconia particles as small as 40 nm could be prepared by using 0.005M of $ZrOCl_2.8H_2O$ and 21.25 micromolar of HPC concentration.

The as prepared amorphous particles of hydrous zirconia crystallized into monoclinic and cubic phases by calcining at 600^0C, 6 hours.

The particle size was not found to change by heating up to 600 C while the surface area changed drastically, i.e. from 90 m^2/gm for washed/dried powder to ~16 m^2/gm upon calcination at 600^{0}C, 6 hours. It is concluded that only the surface pores are sealed off due to heating with the internal porosity remaining intact.

In Conclusion

1. The HPPS instrument was tested and calibrated and was found to yield accurate results.

2. Presence of any adsorbed polymer on the particle surface is likely to produce a larger particle size number by HPPS.

3. Hydrous zirconia powders with particle size down to 40 nm were successfully prepared. The particle size could be varied by varying the ZrOCl$_2$.8H$_2$O concentration.

4. Use of a surfactant such as HPC is very effective in producing dispersed powders. A minimum concentration of the dispersant is needed.

5. Hydrous zirconia particles are most probably porous. This produces powders with high surface area. The surface pores are most probably closed by calcining at 600^{0}C.

6. The as prepared powders can be crystallized by heating to 600^{0}C.

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APPENDIX 1

STEPS IN THE MEASUREMENT BY HPPS

1. First the instrument is switched on and the temperature is allowed to stabilize for 30 minutes.

2. Then HPPS software is started. It is to be noted that after switching on, the software should not be started until the unit beeps twice. If this is not done, then the software will not connect the optical unit.

3. The sample is prepared well (i.e. in well dispersed condition) and the cuvette is filled with the sample upto 10 mm of its height (the maximum height upto which it can be filled should not exceed 15 mm).

4. The cuvette is placed in the sample holder delicately and the lid is closed. Then the temperature is allowed to reach the desired temperature.

5. A new measurement database is created or opened and *manual measurement* is started by selecting *M*easure-*Manual*.

6. Then 'start' button is pressed and the instrument starts to take the measurement.

APPENDIX 2

CALCULATION OF PARTICLE SIZE FROM PHOTOGRAPH

The particle size is calculated from the photograph developed from the negative by using the following formula.

The particle size ϕ is given by

$$\phi = \frac{S \ X \ 4}{M \ X \ m}$$

S = particle size on photograph developed from the negative.

ϕ = actual size of the particle.

M = Magnification at the TEM screen.

m = magnification by which the negative is magnified into a picture.

In the present calculation the value of 'm' is maintained 5.4 in every cases (except calculation of particle size of 0.005M sample, in this case value of m was taken as 8.4).

PARTICLE SIZE DISTRIBUTION ANALYSIS FROM PHOTOGRAPHS

Calculation of mean particle size and standard deviation of hydrous zirconia in case of 0.01M, 1.7H [Fig 3.2.3 (a)] for example is described in the following:

$$\text{Mean particle size, } \mu_d = \frac{\sum_i n_i d_i}{\sum_i n_i}$$

The particle size and their frequency are as follows:

d_i (mm)	n_i
4.0	36
5.0	76
5.5	4
6.0	45
6.5	2
7.0	19
8.0	11
9.0	3
10	4
12	2
14	1
15	1

$$= \frac{(36 \times 4.0) + (76 \times 5.0) + (4 \times 5.5) + (45 \times 6.0) + (2 \times 6.5) + (19 \times 7.0) + (11 \times 8.0)}{204}$$

$$+ (3 \times 9.0) + (4 \times 10) + (2 \times 12) + (1 \times 14) + (1 \times 15)$$

$$= \frac{1170}{204}$$

$$= 5.73 \text{ mm}$$

$$= 5.73 \times 10^{-3} \text{ m}$$

$$\text{Actual particle size, } \phi = \frac{S \times 4}{M \times m}$$

Here, s = 5.73×10^{-3} m,   M = 80×10^{3},   m = 5.4

By putting all these values in the above equation, it becomes

$$\phi = \frac{(5.73 \times 10^{-3}) \times 4}{(80 \times 10^{3}) \times 5.4}$$

$$= 5.310 \times 10^{-8} \text{ m}$$

$$= 53.10 \text{ nm}$$

Hence,
$$\sigma_d{}^2 = \frac{\sum_i n_i (d_i - \mu_d)^2}{\sum_i n_i}$$

$$= \frac{\begin{aligned}&36(4.0\text{-}5.73)^2 + 76(5.0\text{-}5.73)^2 + 4(5.5\text{-}5.73)^2 + 45(6\text{-}5.73)^2 + 2(6.5\text{-}5.73)^2 + 19(7.0\text{-}5.73)^2 + \\ &11(8.0\text{-}5.73)^2 + 3(9.0\text{-}5.73)^2 + 4(10\text{-}5.73)^2 + 2(12\text{-}5.73)^2 + 1(14\text{-}5.73)^2 + 1(15\text{-}5.73)^2\end{aligned}}{204}$$

$$= \frac{578.2116}{204}$$

$$= 2.83437 \text{ mm}^2$$

$\sigma_d = 1.683$ mm $= 1.683 \times 10^{-3}$ m

$$\text{Standard deviation} = \frac{S \times 4}{M \times m}$$

Here, $S = 1.683 \times 10^{-3}$ m, $M = 80 \times 10^{-3}$, m = 5.4

By putting all these values in the above equation, it becomes

$$= \frac{(1.683 \times 10^{-3}) \times 4}{(80 \times 10^{-3}) \times 5.4} \text{ m}$$

$= 1.558 \times 10^{-8}$ m $= 15.58$ nm.

Therefore, particle size distribution becomes 53.10 ± 15.58 nm. In the present study, for calculation of size distribution, two photographs at different magnification were developed for the same sample and then the average value was calculated.

APPENDIX 3

CONVERSION OF STANDARD DEVIATIONTION TO EQUIVALENT WIDTH AT HALF MAXIMUM

The normal distribution is expressed by the formula

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma_x} \exp\left[-\frac{(x-\mu)^2}{2\sigma_x^2}\right] \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

where, σ_x is standard deviation and μ is mean

At x = μ, this equation becomes,

$$f(\mu) = \frac{1}{\sqrt{2\pi}\sigma_x} \exp\left[-\frac{(\mu-\mu)^2}{2\sigma_x^2}\right]$$

$$\Rightarrow f(\mu) = \frac{1}{\sqrt{2\pi}\sigma_x}$$

At half maximum, $f(x) = \frac{1}{2\sqrt{2\pi}\sigma_x}$

$$\Rightarrow \frac{1}{\sqrt{2\pi}\sigma_x} \exp\left[-\frac{(x-\mu)^2}{2\sigma_x^2}\right] = \frac{1}{2\sqrt{2\pi}\sigma_x}$$

$$\Rightarrow \exp\left[-\frac{(x-\mu)^2}{2\sigma_x^2}\right] = \frac{1}{2}$$

$$\Rightarrow -\frac{(x-\mu)^2}{2\sigma_x^2} = -\ln 2$$

$$\Rightarrow -(x-\mu)^2 = -2\sigma_x^2(-\ln 2) = 2\sigma_x^2 \ln 2$$

$$\Rightarrow (x-\mu) = \pm\sqrt{2\sigma_x^2 \ln 2}$$

$$\Rightarrow x = \mu \pm \sqrt{2\sigma_x^2 \ln 2}$$

Therefore the solution of this equation becomes

$$x_1 = \mu - \sqrt{2\sigma_x^2 \ln 2}$$

$$x_2 = \mu + \sqrt{2\sigma_x^2 \ln 2}$$

Thus knowing μ and σ_x, the values of x_1 and x_2; hence equivalent width at half maximum from standard deviation can be calculated.